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The Far Ultraviolet Absorption Spectra and Ionization Potentials of C_6H_6 and C_6D_6

W. C. PRICE* AND R. W. WOOD, *The Johns Hopkins University*

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The absorption spectra of C_6H_6 and C_6D_6 have been photographed under high dispersion in the region 2000–1000A. The spectra of both substances are very similar. A strong continuous absorption starts fairly sharply around 1840A and gradually weakens out to zero at 1600A. It is followed by a region extending down to about 1360A which contains very strong sharp bands. The strongest of these bands only suffer small shifts to the violet in going from C_6H_6 to C_6D_6. This shift which is due to the change in the difference of zero-point energy between the normal and the excited states reveals the bands to be vibrationless electronic transitions. It was found that these bands could be arranged into two Rydberg series which had approximately the same limit corresponding to an ionization potential of $9.190 \pm .005$ volts for C_6H_6. The ionization potential of C_6D_6 is only about 3×10^{-4} volts greater than that for C_6H_6. All the electronic states are split up into patterns which are believed to be caused by true electronic multiplicity. The excitation is apparently from a nonbonding electron more strongly attached to the carbon atom. The vibrations which accompany the bands are comparatively weak. However for C_6H_6 the following vibration frequencies associated with the excited states were observed. $\omega_1 = 677$ cm^{-1}, $\omega_2 = 968$ cm^{-1}. These become 630 and 926 cm^{-1} for C_6D_6. Tentative assignments of their modes of vibration are made. The bands below 1360A are considerably more diffuse than those previously mentioned and the isotopic shifts to the violet are much larger for these bands. However they are still believed to be vibrationless electronic transitions though they are due to the excitation of an electron which is considerably more bonding than that corresponding to the first ionization potential. A consideration of them enables the approximate value $11.7 \pm .3$ volts to be predicted for the second ionization potential of benzene.

RECENT investigations[1] have shown that the absorption spectra of many polyatomic molecules in the far ultraviolet are comparatively simple. This is especially so when the excitation is that of a nonbonding electron. In such cases very strong bands are obtained which can usually be ascribed as due to vibrationless electronic transitions. These can frequently be fitted into Rydberg formulas the limit of which gives a very accurate value for the ionization potential of the molecule. The general appearance of such a spectrum, if predissociation does not interfere with it is as follows. At the long wavelength end the bands are strong and well separated. As we go to shorter wavelengths the bands become weaker and closer together, eventually converging to a limit from which a continuous absorption starts. This represents the ionization of the molecule. In the case of a nonbonding electron (cp. the methyl halides H_2S etc.) the vibration transitions accompanying the main electronic transitions are very weak. In cases where the excited electron plays some part in the bond (cp. C_2H_2 and C_2H_4) then the accompanying vibration bands are of the same

* Commonwealth Fellow.

[1] W. C. Price, Phys. Rev. **47**, 444 (1935); J. Chem. Phys. **3**, 256 (1935).

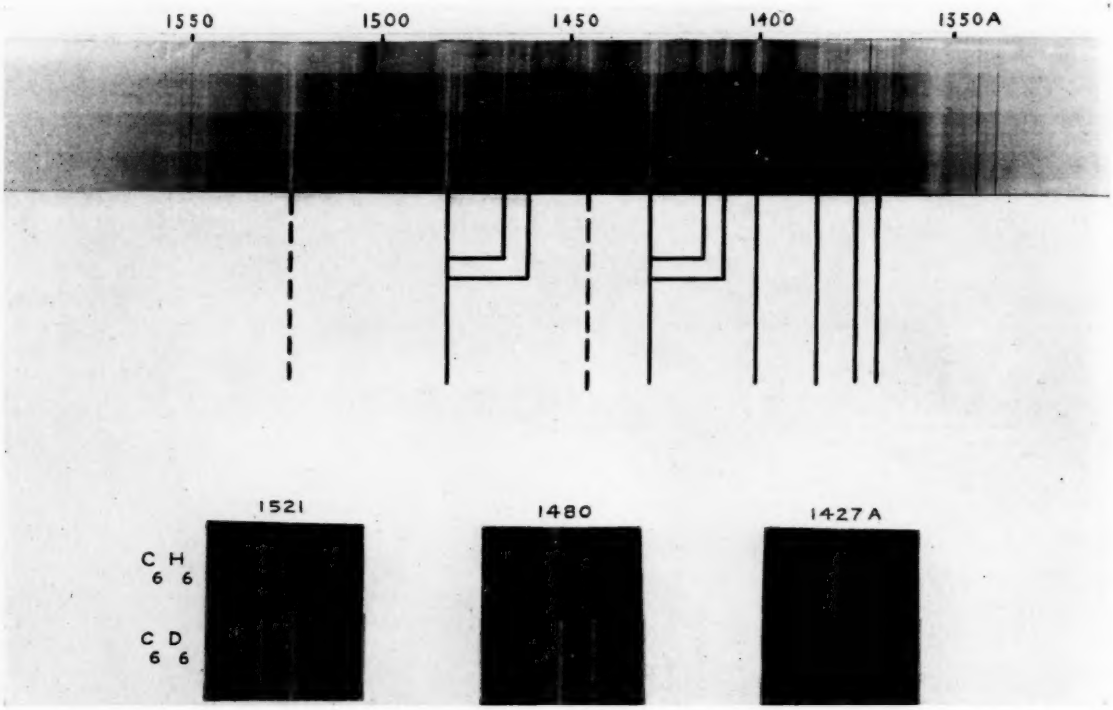

FIG. 1. The far ultraviolet absorption spectrum of benzene.

order of intensity as the band corresponding to the main electronic transition. The absorption coefficients of bands of the type described above are enormously greater than those for visible or near ultraviolet bands as they correspond to electronic transitions of the highest probability. Most of the bands can usually be obtained with pressures of the order 0.01 to 0.1 mm in an absorbing column of about a meter. It may be remarked here that the first few absorption spectra observed in this region (i.e., the Dieke and Hopfield bands in hydrogen and Hopfield's bands in N_2 and CO) are not of the type described here and furthermore these bands come out at somewhat higher pressures.

The far ultraviolet absorption spectrum of benzene may now be considered in the light of the previous remarks. It was obtained in the following manner. A vacuum spectrograph of the grazing incidence type having a dispersion of about 2.3A/mm was used. The Lyman continuum which was obtained from a discharge tube of the type designed by Collins and Price[2] served as a background against which the absorption could be observed. Hydrogen or helium was used as a conducting gas in the discharge tube. The benzene vapor was admitted into the body of the spectrograph and pumped out through the main evacuating pump. Thus the path length in which the absorption took place was that between the slit and the grating, and the grating and the photographic plate. This distance amounted to about 1.5 meters in the particular instrument used here. The partial pressures of benzene present in the spectrograph during an exposure were around 0.1 mm. It was admitted into the spectrograph in small quantities (i.e., volumes of about 15 cc at 10 cm pressure) at frequent intervals of time. The huge volume of the spectrograph which was about 180 liters smoothed out the pressure of the benzene so that it remained sensibly constant throughout the exposure which usually lasted about an hour. Lines in the spectrum of molecular hydrogen were used as standards. Their wavelengths were taken from Hyman.[3]

[2] Collins and Price, Rev. Sci. Inst. **5**, 423 (1934).

[3] H. H. Hyman, Phys. Rev. **36**, 187 (1930).

Under the conditions described above the absorption spectrum shown in Fig. 1 was obtained. It consists of a strong continuous absorption starting fairly sharply around 1840A. This gradually weakens out and at 1600A its intensity becomes almost zero. Below this a set of very strong discrete bands appears. These are quite narrow and are only slightly degraded towards the red. They get weaker and closer together as we go to shorter wavelengths and eventually merge into a weak continuum around 1360A. Superimposed on this continuum the first members of another set of fairly strong diffuse bands start. Similar bands which are related with these also appear at shorter wavelengths. A great deal could not however be done with them on account of their predissociation and the weakening of the continuum by some general absorption.

The opportunity of studying the absorption spectrum of C_6D_6, a small quantity of which was kindly provided by Professor H. S. Taylor of Princeton University, threw considerable light on the nature of the bands and confirmed an analysis of the spectrum of light benzene which had previously been made by one of us.

Enlargements of a small region of the photographs of both light and heavy benzene are also shown in Fig. 1. The spectra are lined up by the emission lines in the continuum. It can be seen from this photograph that the sets of bands obtained in both light and heavy benzene are essentially similar. However, those of the latter suffer a small shift to the violet relative to those of the former. The magnitude of this shift, which is only about 30 cm^{-1} makes it certain that the bands are mainly due to vibrationless electronic transitions. It can be shown that such a shift is accounted for by the change of the difference in zero-point vibrational energy between the ground state and the excited state as we go from C_6H_6 to C_6D_6. It is given by an expression

$$\tfrac{1}{2}\{\Sigma(\omega''-\omega^{*''})-\Sigma(\omega'-\omega^{*'})\}.$$

ω and ω^* refer to C_6H_6 and C_6D_6, respectively. $''$ refers to the ground state and $'$ to the excited state. If the vibration frequencies are diminished by the excitation then this shift is positive.

When the frequencies of the strongest bands of the little pattern which accompanies all the bands were taken, it was found that they could be expressed in two Rydberg series going to approximately the same limit. This limit corresponds to an ionization potential of $9.190\pm.005$ volts. Unfortunately there appears to be no value of the ionization potential of C_6H_6 determined by the methods of electron impact with which to compare this value. However, the degree of accuracy with which the bands are represented by Rydberg formulas coupled with the facts that they all suffer small shifts to the violet due to zero-point energy changes; that similar patterns accompany each member of a particular series; and the intensities of the bands fall off with increasing quantum number in the manner expected for electronic series make it certain that this is a true ionization potential. Further arguments that could be brought forward are that benzene is expected to have ionization potentials in the range 8–12 volts (cp. C_2H_2, C_2H_4, C_2H_6[1]); that these bands are by far the strongest bands which appear in this region and they come out at such pressures which previous experience has shown to be the usual pressures at which bands going to an ionization potential appear. The Rydberg formulas to which the two sets of bands conform are:

$$\nu_0^n = 74{,}495 - R/(n+.97)^2, \quad (1)$$
$$\nu_0^n = 74{,}590 - R/(n+.55)^2 \quad n=3,\ 4,\ 5,\ \text{etc.} \quad (11)$$

An idea of the accuracy with which these formulas represent the bands may be obtained from an inspection of Table I. The accuracy of

TABLE I. *Table showing the observed and calculated frequencies of the C_6H_6 bands of series (1) and (11) along with the bands of C_6D_6 and the isotopic shifts.*

			Series (1)			
n	I	ν obs. C_6H_6	calc.	I	ν obs. C_6D_6	Isotopic shift
3	10	67529	67535	10	67562	33
4	10	70047	70052	10	70075	28
5	9	71415	71416	9	71447	32
6	8	72242	72236	8	72275	33
7	5	72777	72767	3	72807	30
8	3	73124	73136			
			Series (11)			
n	I	ν obs. C_6H_6	calc.	I	ν obs. C_6D_6	Isotopic shift
3	10	65716	66882	10	65746	30
4	8	69273	69289	7	69312	39
5	blend	71025	71027	3	71061	36
6	2D	72035	72032	2	72075	40
7	1D	72668	72665			

D = diffuse.

the measurements is such that the frequencies given are probably correct to within ten wave numbers.

The first member of series (11) is somewhat off the series but this is to be expected as large dipole effects are present and the bands should only approximate to Rydberg series for the higher quantum numbers. Another difficulty with series (11) is that the bands fall off rapidly in intensity and also that some of them are obscured by overlapping. The bands used in the series are the strongest bands in the little pattern which accompanies each main electronic transition. In fact, the spectrum might best be described by saying that the bands occur in patterns. This appears to be a more or less unique feature of the spectrum of C_6H_6 and has not been observed to the same extent in any of the other molecules investigated in this laboratory. We will postpone further discussion of this pattern until we have dealt with two vibration frequencies which were found to accompany all the strong electronic transitions.

The ω_1 and ω_2 Vibrations

To the short wavelength side of all the strong patterns, two very much weaker patterns were observed at distances of ~ 677 cm^{-1} and 968 cm^{-1} from the corresponding strong pattern (*vide* Table III). As is indicated in Fig. 2 these patterns are identical with the particular pattern they accompany. This is so within the error of measurement. These frequencies become about 630 cm^{-1} and 926 cm^{-1} for C_6D_6. They will be here designated as the vibrations ω_1 and ω_2. ω_2 undoubtedly corresponds to the Raman frequency of 991 cm^{-1}. The small difference between the value in the excited state and that in the normal state is in harmony with the fact that the isotopic shifts due to changes in zero-point energy are small. Combined with the fact that these vibrational transitions are much weaker than the main electronic transition, this becomes strong evidence that the electron is of a non-bonding type. It seems very probable that ω_2 corresponds to the type of vibration given as 1 by Wilson[4] or type *H* by Teets and Andrews.[5]

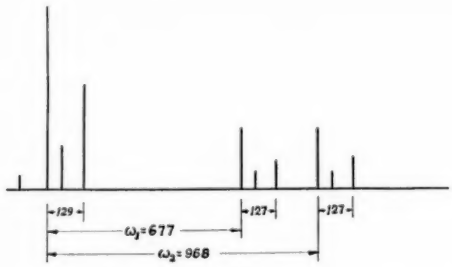

FIG. 2. Diagram of band at λ1427.6 showing the weak vibrations ω_1 and ω_2 accompanying it.

At least this is the assignment given to the 991 frequency of the ground state by the latter authors. It is supported by the isotope factor which is only a little less than $(13/14)^{\frac{1}{2}}$ and is just what would be expected if the carbon and hydrogen atoms move together along the radii. A more detailed calculation[6] involving plausible assumptions with regard to the force constants between the atoms enables the isotope shift to be predicted fairly exactly if this mode of vibration is assumed. The symmetry of the vibration is such that its appearance would not be forbidden in the spectra obtained here. It is interesting to note that it also appears in the near ultraviolet bands[7] though as is usual in these bands its frequency is somewhat more greatly modified becoming about 928 cm^{-1}.

The value of ω_1 in the ground state is also probably not a great deal different from its value of 680 cm^{-1} in the excited state. It cannot be associated with the nearest Raman lines at 849 and 605 cm^{-1} (662 and 581 for C_6D_6)[8] on account of the difference in the isotope factors. Thus it is most likely a vibration whose appearance in Raman spectra and the infrared is in some way forbidden. This is also true of the 162 frequency associated with the ground state by Henri from an analysis of the near ultraviolet bands. In fact, these two vibrations may be the two that are necessary to complete the vibration scheme for benzene. Twenty independent modes of vibration are predicted by Wilson and eighteen have so far been found in Raman spectra and the infrared. ω_1 may well correspond to the type of

[4] E. B. Wilson, Jr., Phys. Rev. **45**, 707 (1934).
[5] D. E. Teets and D. H. Andrews, J. Chem. Phys. **3**, 175 (1935).
[6] Murray, Squire and Andrews, J. Chem. Phys. 2, 714 (1934).
[7] V. Henri, J. de phys. et rad. **9**, 249 (1928).
[8] R. W. Wood, article in this issue.

vibration designated as *D* by Teets and Andrews. At least this satisfies the requirement of the isotopic shift which is that the vibration should be mainly among the carbon atoms, the hydrogens merely following the carbons with which they are associated. This mode of vibration should also correspond to a fairly low frequency in agreement with what is found (i.e., it is a vibration in a carbon-carbon bond which is modified by the additional mass of the rest of the ring).

We have now to discuss the patterns which accompany all the bands. The pattern for series (1) is composed of two strong bands and two weak bands. That for series (11) is mainly one strong band which is accompanied by one or two weak bands to the long wavelength side of it. The patterns for subsequent electronic states of the same series resemble one another in a general way (i.e., the corresponding bands in the pattern can be easily picked out). However, there does not seem to be any simple relation between the members of the patterns except that they get closer together with increasing quantum number. An idea of the frequency differences which are associated with the patterns may be obtained from Table II. It does not seem probable that any of the small differences associated with a particular pattern correspond to vibration frequencies. Some of them are of such intensities as virtually to demand more than two members of a vibrational progression which were certainly not found in our case. No exact regularity could be found in them in passing from one state to another. The accuracy of measurement was far greater than that necessary to establish such a regularity. Nothing could be gained from the isotope shifts in the patterns as these were sometimes such that the differences were increased not diminished by the substitution of the heavy isotope. It remains therefore for us to suggest rather cautiously that the pattern is caused by some multiplicity of the electronic states. This would at least take care of the increase in the dimensions of some of the patterns by the substitution of the heavy isotope. The apparent anomaly can be then accounted for by the difference in change of zero-point energy of the two different excited electronic states. The force constants would not be the same and thus the vibrations involved in the zero-point energy would be affected to a different extent.

Most of the bands observed above 1360A are given in Tables I, II and III. All the bands of appreciable intensity are accounted for in this analysis.

TABLE II. *Table of frequencies for the various band patterns.*

			Series (1)			
n	*I*	ν obs.	$\Delta\nu$	*I*	ν^* obs.	$\Delta\nu$
3	2	67429		4	67466	
			100			96
	10	529		10	562	
			74			115
	3	603		3D	677	
			81			97
	6	684		9	744	
4	3	69947		2D	69988	
			100			87
	10	70047		10	70075	
			49			52
	4	096		5	127	
			80			73
	6	176		6	200	
5	2D	71334		2D	71367	
			81			80
	9	71415		9	447	
			42			37
	7	457		6	485	
			56			53
	6	513		5	538	
6	1	72186				
			56			
	8	242		8	72280	
			37			35
	7	279		6	315	
			45			49
	3	324		4	364	
			Series (11)			
n	*I*	ν obs.		*I*	ν^* obs.	
3	2D	65540		3	65582	
			84			87
	4D	626		5	669	
			90			77
	10	716		10	746	
4		—			—	
	2D	69183		1	69224	
			90			88
	8	273		7	312	

— refers to bands too weak to be observed.

TABLE III. *Table showing derivation of* ω_1, ω_2, *and* ω^*_1, ω^*_2.

n	*I*	ν	*I*	$\nu+\omega$	ω	*I*	ν^*	*I*	$\nu^*+\omega^*$	ω^*
3	10	67529	4	68208	679	10	67562	3	68205	643
			4	495	966			3	483	921
	6	684	2	348	664	9	774		—	—
			2	646	962				—	—
4	10	70047	4	70725	678	10	70075	3	70711	636
			4	71017	970			2	71003	928
	4	096	2	70774	678	5	127	2	70762	635
			2	71066	970			2	71061	934
	6	176	2	70852	676	6	200	2	70826	626
			2	71144	968			2	71124	924
5	9	71415	3	72092	677	9	71447	2	068	621
			3D	383	968			1D	367	920
	7	457	2	134	677	6	485	1	120	635
			2	423	966					
	6	513	1	188	675	5	538			
			2D	477	964			b	447	911
6	8	72242	2	911	669					
			2	73211	969					
	7	279	2	72946	667					

* refers to C_6D_6. D = diffuse. b = blend.

Below 1360A a new set of somewhat diffuse bands starts. The first member, which is partly in the ionization continuum of the above set, is very strong. It is shifted to the violet by quite a large amount ($\sim$285 cm^{-1}) by the change from C_6H_6 to C_6D_6. It is believed that the transition is still a vibrationless electronic transition but that the electron is in this case a more strongly bonding one (i.e., its removal diminishes the vibration frequencies of the molecule considerably). This band is followed by some very weak diffuse bands and a certain amount of general absorption. The next bands which are of sufficient intensity to be linked with it as subsequent members of an electronic series occur around 1180A. These also suffer isotopic shifts to the violet of the same order of magnitude. Unfortunately general absorption made it difficult to observe higher members of this electronic series, nevertheless it is felt fairly safe to estimate the second ionization potential of benzene to be 11.7 ± 0.3 volts.

The first ionization potential given here must obviously be that of an electron more strongly attached to a carbon atom. It is interesting to note that its value is considerably lower than the first ionization potentials of C_2H_2, C_2H_4, or C_2H_6 (11.36, 10.41 and $\sim$12 volts) which are also due to electrons mainly associated with the carbon atoms. In these cases however, the electrons contribute considerably toward the bond. The low ionization potential observed in benzene may be partly caused by a large charge transfer or dipole effect in the phenyl group. It may also be brought about by the resonance which would predict one high and one low ionization potential.

In conclusion the authors wish to express their indebtedness to Professors G. H. Dieke and K. F. Herzfeld for their suggestions with regard to the material of this article and to Professor H. S. Taylor of Princeton for making the heavy benzene available.

Note added in proof: To obtain strong electronic series going to an ionization potential it is necessary that the character of the ion be opposite to that of the normal molecule (i.e., $g\rightarrow u$ or $u\rightarrow g$). It is thus most probable that a "p" electron is excited.

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Raman Spectrum of Benzene-d_6

R. W. Wood, *The Johns Hopkins University*

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THE sample of heavy benzene, 1.5 cm^3, was supplied by Professor H. S. Taylor of Princeton. It was contained in a straight tube 30 cm in length and 6 mm internal diameter closed at one end with a disk of optical Pyrex, and sealed at the other end. The tube was wrapped with insulation tape with the exception of a length of 4 cm near the window, and was mounted in a vertical position, with a right-angle total reflecting prism a short distance below the window.

A 220-volt Hanovia quartz mercury arc in its metal housing, turned into the vertical position, was employed for the excitation. The sliding metal plates were removed from the box, securing perfect ventilation, and the light which emerged from the vertical slot opposite the burner was focused on the benzene tube with a cylindrical lens consisting of a glass tube 4 cm internal diameter, and 40 cm long, half full of a strong solution of sodium nitrite (for excitation by 4358) or of iodine in carbon tetrachloride for excitation by 4046, as described in a previous paper.[1] This method of operating the illuminating system obviates the necessity of the ventilating fan as described in an earlier paper. The lower portion of the tube, which contains the fluid benzene is backed by a concave cylindrical reflector of thin sheet aluminum and the lamp moved into such a position that the direct and reflected cones of scattered light coincide on the axis of the tube, as viewed in the prism.

The first photograph taken showed a strong continuous background and only one line distinctly, though faint traces of other lines appeared. Having eliminated this troublesome fluorescence in the case of the heavy water,

[1] Wood, Phys. Rev. **38**, 2169 (1931).

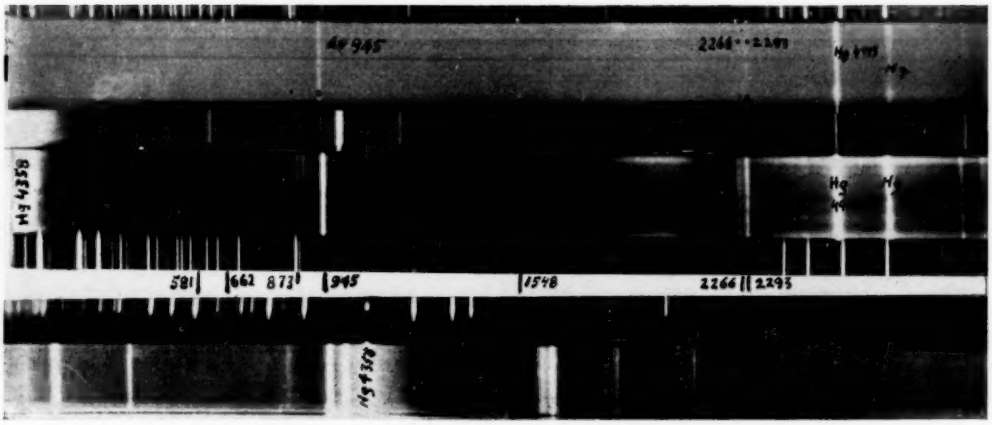

FIG. 1.

obtained from the same laboratory, by a 48-hour exposure to ultraviolet light, I substituted water for the sodium nitrite and exposed the benzene to the full radiation of the lamp for 24 hours. The fluorescence was practically destroyed and excellent Raman spectra immediately secured.

The upper spectrum in Fig. 1 is the one taken before the fluorescent impurity had been destroyed (Raman lines marked with dots) the middle spectrum of ordinary benzene, and the lower of heavy benzene.

The $\Delta\nu$ values of both benzenes are given in Table I.

Corresponding lines of the two benzenes have been placed opposite each other. The shift of the 1178 line to 873 makes it appear out of place in the spectrum with respect to 991 which is shifted only to 945. The doublet 1584–1606 is fused to a single line at 1548. Both of these phenomena were predicted from theory by E. Bright Wilson (communicated by letter). The lines 605 and 849, of very different intensities with ordinary benzene have the same intensity with heavy benzene. Wilson's predictions of the shifts were closely confirmed.

TABLE I.

C_6I_6	C_6D_6	C_6H_6	C_6D_6	
605	581	2947		
849	662	3042	2266	
991	945	3062	2293	
	1000 (faint)	3157	2575	
1178	873	3176	2617	doubtful
1584 }	1548		2663	doubtful
1606 }		3573	3052	
	2031 (broad, faint)	3627	3108	

With the heavy benzene a distinct pair of lines was found very near the point at which the strong doublet 3042–3062 is found with ordinary benzene. The $\Delta\nu$ values for these lines were 3052 and 3108, and they were found both by 4046 and 4358 excitation. They are shown on the lowest spectrum obtained by 4046 excitation at the extreme right marked by dots. This made me suspect that a careful search might reveal the corresponding lines for ordinary benzene, with $\Delta\nu$ values of over 3500, though no lines of such large $\Delta\nu$ value have ever been recorded.

A spectrum of a very pure thiophen-free benzene was made with 4358 excitation and an Eastman green sensitive plate, and a pair of lines found at wavelengths 5162 and 5177, giving $\Delta\nu$ values of 3573 and 3627, and as no mercury lines were found at this point, I feel very certain that the lines are real. I was unable to obtain them with 4046 excitation, but the continuous background was stronger in this case. That they have not been observed previously is probably due to the fact that they are in the region of lowest sensitivity of most photographic plates.

The lines 2617 and 2663 (marked doubtful) were obtained with iodine filtered 4046 excitation, the latter coinciding with $\Delta\nu$ 945 excited by 4348 and the former nearly in coincidence with $\Delta\nu$ 945 excited by 4339. The circumstance that $\Delta\nu$ 945 excited by 4358 was rather faint makes it seem possible that the two lines are real. They are marked with interrogation marks on the lowest spectrum. Just to their left is the 2575 line, faint but undoubtedly real.

The Near Infrared Spectrum of Benzene-d_6

R. Bowling Barnes and R. Robert Brattain, *Palmer Physical Laboratory, Princeton University, Princeton, N. J.*

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The transmission spectrum of C_6D_6 has been studied from 1μ to 13.25μ and the shifts of three of the four infrared active vibrations determined. The results obtained are in substantial agreement with the assumption of a plane symmetrical molecule as outlined by Wilson. Measurements on C_6H_6 and thiophene extending from 1μ to 15μ are also presented.

ACCORDING to present theoretical considerations[1] the benzene molecule is best represented by a regular plane hexagon model with the carbons and hydrogens all lying in the same plane. Of the thirty possible modes of vibration of such a model only four are infrared active. These have been observed and carefully studied by many investigators and are found at 3.25, 6.75, 9.78 and 14.90μ, respectively. In addition to these fundamentals several other weaker bands are usually found, which are thought of as combination bands.

With the advent of heavy hydrogen it was immediately evident that infrared measurements upon molecules prepared from it would furnish important data concerning the structure of these molecules. This has been shown to be true by the work of various authors in which the vibrations and in some cases the rotations of heavy methane, ammonia, acetylene, etc., have been studied. As a result of these successes we were particularly glad to receive from Professor Taylor a sample of heavy benzene prepared as described in a previous paper,[2] and to be able to measure its near infrared spectrum. Since a discussion of the theoretical significance of these measurements with regard to the general properties and the structure of the benzene molecule is to be presented in a subsequent paper by Dr. Benedict and Mr. Bowman, the present paper will be concerned only with the experimental side of the problem.

The chief purpose of this investigation was to map the positions of the vibration bands of C_6D_6 with particular reference to the frequencies corresponding to the four active vibrations of C_6H_6 mentioned above. From a comparison of these observed values with those calculated by Benedict, the validity of the present assumptions regarding the ordinary benzene molecule may be

TABLE I. *Observed and calculated frequencies of C_6H_6 and C_6D_6.*

C_6H_6		C_6D_6		
λ in μ (Obs.)	ν in cm^{-1} (Obs.)	λ in μ (Obs.)	ν in cm^{-1} (Obs.)	ν in cm^{-1} (Calc.)
0.84	11,905	1.01	9901	
1.08	9259	1.375	7272	
1.25	8000	1.56	6410	
1.65	6061	1.90	5263	
2.03	4926	2.28	4386	
2.35	4255	2.88	3472	
2.75	3636	3.06	3268	
3.25	3077	3.20	3125	
3.75	2667	3.55	2817	
4.00	2500	3.95	2532	
4.45	2247	4.36	2294	2310
5.15	1942	5.18	1930	
5.60	1786	5.45	1835	
6.02	1661	5.70	1754	
6.18	1618	6.03	1658	
6.77	1477	6.22	1608	
7.32	1366	6.95	1439	
7.91	1264	7.57	1321	1320
8.35	1198	8.09	1236	
8.65	1156	8.72	1147	
8.94	1119	9.25	1081	
9.17	1090	9.47	1056	
9.76	1025	9.89	1011	
10.46	956	10.15	985	
10.67	937	10.46	956	
10.95	913	10.70	935	
11.20	893	10.85	922	
11.32	883	11.13	998	
11.66	858	11.45	873	
11.86	843	11.56	865	
11.97	835	11.96	836	
12.07	829	12.20	820	
12.22	818	12.38	808	
12.41	806	12.55	797	817
12.64	791	12.76	785	
12.75	784	13.04	767	
12.91	775			
13.02	768			
13.35	749			
13.60	735			
13.90	719			
14.14	707			
14.41	694			
14.70	680			
14.95	669			4

[1] E. Bright Wilson, Jr., Phys. Rev. **45**, 706 (1934).
[2] Bowman, Benedict and Taylor, J. Am. Chem. Soc. **57**, 960 (1935).

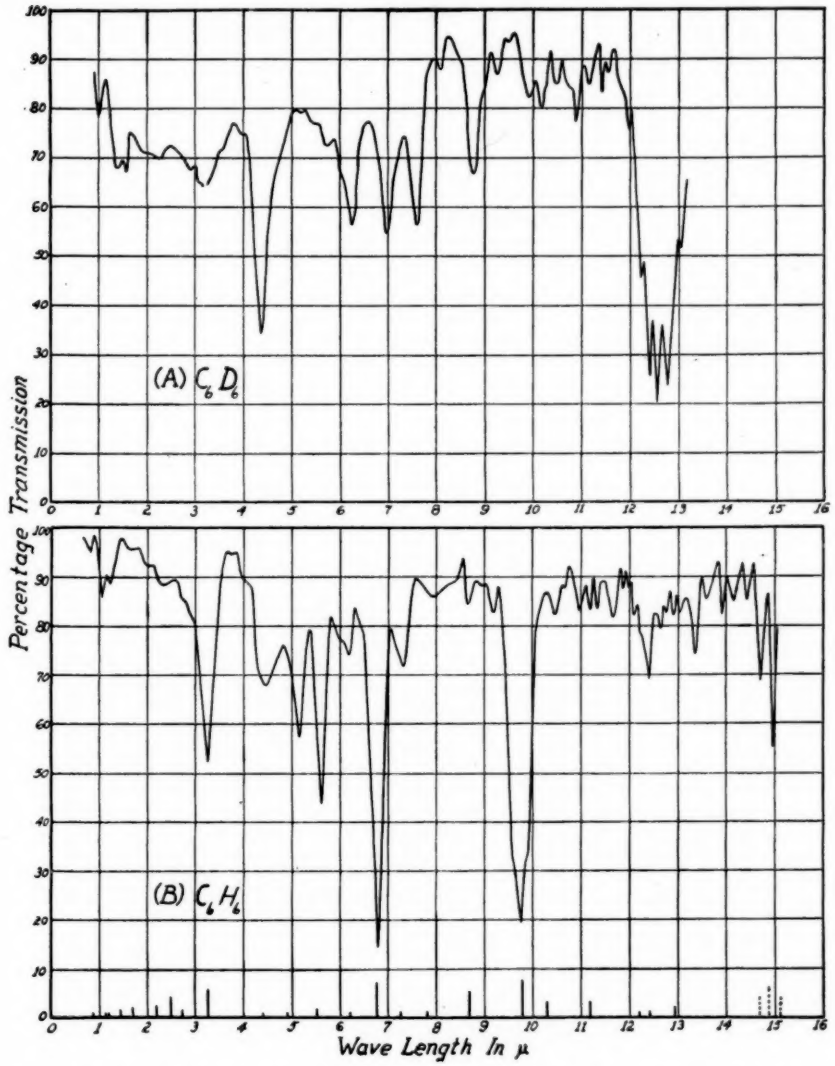

FIG. 1. Comparison of the near-infrared spectra of light and heavy benzene. (*a*) C_6D_6 (*b*) C_6H_6. The vertical lines in (*b*) show the positions and intensities of the absorption bands as given by Coblentz. The group around 15μ are by Kettering and Sleator.

tested. At the present time the fine structure of these bands was not considered, hence a rocksalt spectrometer employing a 60° prism and 40 cm focal length mirrors was used. The slits were kept 0.35 mm wide throughout all of the measurements, some 10 to 20 points being taken to each μ. The source was a hot platinum strip operated at 20 amperes by a 22-volt transformer and the receiving device a Moll linear thermopile connected to a photo-relay system.

The gas was contained in a 15 cm glass cell having rocksalt windows. The cell was filled by placing a few drops of the liquid in a side tube, freezing it with liquid air, evacuating the cell and then removing the liquid air. The percentage transmission of the benzene was arrived at by employing the following procedure. First a complete run was taken throughout the entire spectral range, in which readings were taken of the filled cell against the energy. These gave the percentage transmission of the cell plus the benzene. The latter was then frozen out completely and a similar run taken in order to get the percentage transmission of the cell alone. Upon making the

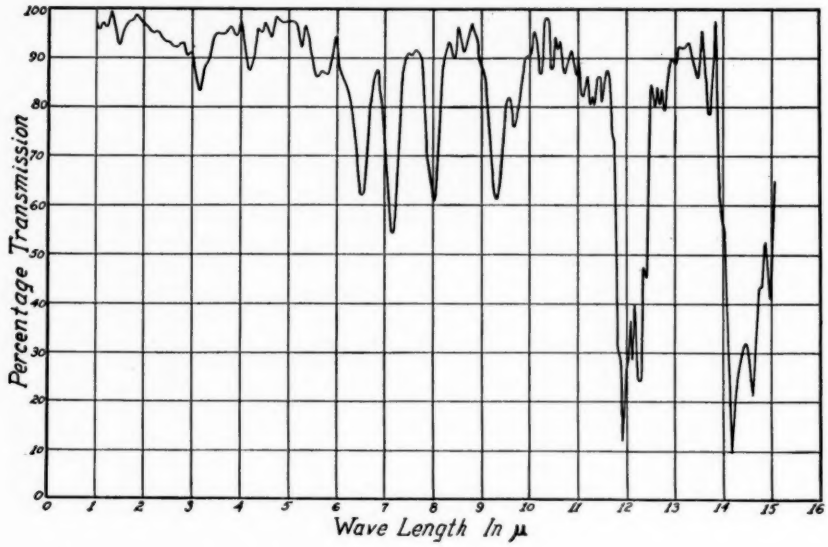

FIG. 2. Near-infrared spectrum of thiophene.

proper corrections the transmission of the benzene alone was then obtained. No experimental points are shown in the curves, the values given being the averages of several runs. No absorption band has been indicated which has not been found on at least two separate runs.

In order to complete the story similar measurements were made upon ordinary benzene, in spite of the fact that these values are well known.* The sample used was furnished us by Mr. Bowman and was the same benzene from which the C_6D_6 was prepared. Thiophene, C_4H_4S, is very hard to remove from benzene and so, although we did not suspect its presence in our benzene, a careful run was made on pure thiophene in order to be sure that none of the bands came from this source. The results showed that the benzene was thiophene free.

The instrument was calibrated empirically, by locating carefully the well-known absorption bands of H_2O, CO_2 and the reflection bands of SiO_2. This calibration curve was then checked by mapping the spectra of toluene cyclo-hexane and cyclo-hexene. None of the known bands of these substances was off by as much as 0.10μ. All of the values listed in Tables I and II are probably accurate to $\pm 0.05\mu$. In each of the curves, every minimum which was found to agree in the separate runs taken upon that substance was plotted. The interpretation of the weak bands is uncertain.

In Fig. 1, curve (a) shows the C_6D_6 results. This series of measurements was extended only as far as 13.25μ, since the calculated values indicated

TABLE II. *Observed frequencies of C_4H_4S.*

C_4H_4S		C_4H_4S	
λ in μ (Obs.)	ν in cm^{-1} (Obs.)	λ in μ (Obs.)	ν in cm^{-1} (Obs.)
1.10	9091	9.67	1034
1.25	8000	10.00	1000
1.50	6667	10.23	978
1.75	5714	10.45	957
2.20	4545	10.57	946
2.45	4082	10.71	934
2.67	3745	10.97	912
2.91	3436	11.08	903
3.18	3145	11.25	889
3.35	2985	11.28	887
3.65	2740	11.50	870
3.92	2551	11.92	839
4.19	2387	12.13	824
4.45	2247	12.27	815
4.65	2150	12.41	806
4.87	2053	12.59	794
5.27	1898	12.69	788
5.59	1789	12.80	781
5.82	1718	13.01	769
6.52	1534	13.17	759
7.16	1397	13.46	743
7.56	1323	13.72	729
8.01	1248	14.19	705
8.43	1186	14.61	684
8.64	1157	14.77	677
9.32	1073	14.98	668

* Schaefer and Matossi, *Das Ultrarote Spectrum* (Breslau, 1930).

that the fourth fundamental would lie around 20μ, which was beyond the limit of our instrument. The measurements on C_6H_6, curve (b), were extended only as far out as 15.05μ since this was very near the limit of our instrument and since the wavelength of this last absorption was well known. The vertical lines at the bottom of the graph give the wavelengths and intensities as listed in *Das Ultrarote Spectrum*. The agreement of these two sets of data is very good, however attention is called to several new bands in our curves and to the large discrepancy in the intensities of the band at 8.65μ. A comparison of curves (a) and (b) shows the absence of C_6H_6 in the C_6D_6, in complete agreement with the results of the ultraviolet measurements to be discussed in a later paper. The good agreement between the observed and calculated frequencies of the fundamentals of C_6D_6 is, as will be shown below, excellent support for the present theoretical assumptions concerning the structure of the benzene molecule. Table I presents a summary of the benzene results. The calculated values are by Benedict.

In Fig. 2 and Table II the results on a sample of Eastman Kodak thiophene are presented.

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The Raman Spectra of Arsenic Trichloride and of Its Mixtures

A. E. Brodskii and A. M. Sack, *Institute of Physical Chemistry, Dnepropetrowsk, U. S. S. R.*

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The Raman spectra from mixtures of $AsCl_3$ with benzene, carbon tetrachloride, methyl and ethyl alcohol have been investigated. The strong deviations from additivity have been observed for $AsCl_3$ in alcohols. The shifts are correlated with the strength of the bond As—Cl. A computation of the constants of the molecule $AsCl_3$ is made which agrees with electronographic data. The geometrical configuration of the molecule $AsCl_3$ in mixtures undergoes only a slight deformation, but the bond As—Cl is considerably weakened in alcoholic solutions.

1.

INVESTIGATION of Raman spectra of liquid mixtures did not give definite results. In certain cases, the spectrum of mixtures is a strict superposition of the spectra of the components,[1] in other ones various changes have been observed, e.g., the splitting of Raman lines, their shifts and the variation of relative intensities, the disappearance of some frequencies or the appearance of new ones.[2] These deviations from additivity are ascribed to polymerization, to formation of complexes or to solvation. Up to now it has not been possible to establish a clearly expressed connection between the deviations of Raman spectra of mixtures from additivity and the properties of the components of the mixture. In particular, there is no parallelism between deviations from additivity and dipole moments:[3] in certain cases the mixtures with dipole components behave additively, in others additivity is broken in the presence of nonpolar components of the mixture. The question requires thus additional experimental research.

We have examined the Raman spectra of mixtures of arsenic trichloride with benzene, carbon tetrachloride, methyl and ethyl alcohols. The method and detailed results for the two

[1] A. Dadieu and K. W. F. Kohlrausch, Physik. Zeits. **30**, 384 (1929); E. H. L. Meyer, ibid. **32**, 293 (1931); R. E. Whiting and W. H. Martin, Trans. Roy. Soc. Canada **25**, 87 (1931); E. A. Crigler, Phys. Rev. **38**, 1387 (1931); H. H. Voge, J. Chem. Phys. **2**, 264 (1934); S. Leitmann and S. Uchodin, Comptes rendus Acad. USSR **4**, 14 (1934).

[2] A. Dadieu and K. W. F. Kohlrausch, Wien. Ber. **138**, 335 (1929); **139**, 77, 439 (1930); **140**, 293 (1931); E. H. L. Meyer, reference 1; P. Krishnamurti, Ind. J. Phys. **6**, 401 (1931); S. Parthasarths, ibid. **6**, 287 (1931) etc.

[3] For once, such a parallelism was observed for HCl in dipole solvents (W. West and P. Arthur, J. Chem. Phys. **2**. 215 (1934)).

former mixtures were published before,[4] the results for the two latter ones are to appear soon.[5] The accuracy of measurement of the spectra is 1–2 cm^{-1} for sharp Raman lines, for diffuse ones it is reduced to 5 cm^{-1} and less.

The frequencies of benzene, carbon tetrachloride and of both alcohols suffer no changes in mixture with arsenic trichloride. Inversely, the frequencies of the latter are somewhat displaced in the former two solvents, and two of them (372 and 410 cm^{-1}) decrease sharply in alcohols, approximately by the same value (25–30 cm^{-1}) and apparently having no dependence on the concentration (10–50 percent by weight $AsCl_3$). In Table I are represented the

TABLE I.

	$AsCl_3$	$AsCl_3$ $+C_6H_6$	$AsCl_3$ $+CCl_4$	$AsCl_3$ $+CH_3OH$	$AsCl_3$ $+C_2H_5OH$
I.	159	153	153	154	159
II.	195	191	187	198	198
III.	372	369	382	348	342
IV.	410	401	408	389	388

final average results for the frequencies of $AsCl_3$ in the four mentioned mixtures and in the pure state. For the latter one our measurements are in good agreement with the previous results of other authors.[6]

Thus, in mixture with arsenic trichloride both the nonpolar C_6H_6 and CCl_4 and alcohols, which possess a considerable moment ($M=1.68$ and 1.74×10^{-18}) suffer no change of their own frequencies. At the time, as the former two have an insignificant influence upon the proper frequencies of $AsCl_3$, the second ones displace them strongly. If we assume these displacements to be due only to the dipole moments of alcohols, it is not clear why the frequencies of the latter are not also displaced in the presence of $AsCl_3$ which possesses a considerable moment.[7] The presence of a considerable moment appears thus as a necessary but insufficient condition for shifts of the frequencies. It is plausible to assume as a second necessary factor a comparatively weak bond between those parts of molecules which participate in active vibrations. While for the vibrations which define the Raman spectra of benzene and alcohols, the elastic constant of bond lies between $4.3-6.3\times10^5$ dyne/cm and for CCl_4 it is 2.0×10^5 dyne/cm,[8] for vibrations As−Cl in $AsCl_3$ it has only a value 1.7×10^5 dyne/cm.[9] The energy of the bond As−Cl (about 65 Cal.) is also less than the bond-energies in molecules of the solvents for $AsCl_3$ which were studied by us.

The fact that Trumpy[10] has found considerable shifts in the mixtures of dipole halides for both components can be considered as an indirect corroboration of our assumption. Also in these compounds both the elastic constants and the bond energies are considerably smaller than in benzene, carbon tetrachloride and alcohols.[11]

Thus, in mixtures we must expect especially considerable shifts of those frequencies which correspond to the weakest bonds in the presence of a considerable dipole moment for the second component of the mixture. The material given below will show to what extent this conclusion from our observations has a general character.

2.

In order to compute the constants, by which the molecule $AsCl_3$ is characterized, one must proceed from a regular trihedral pyramid, with ion As^{+++} at its top and with ions Cl^- at the bases. Assuming central forces, the computation can be made according to Dennison's equations.[12] The results of the calculation depend upon the way in which the observed frequencies are correlated with possible modes of vibration. We have proceeded from the following assignment of frequencies: $\omega_1=410$, $\omega_2=159$, $\omega_3=372$ and $\omega_4=195$, where ω_1 and ω_2 are the single vibrations along the symmetry axis and ω_3 and ω_4 are the double vibrations perpendicular to it.

[4] A. E. Brodskii, A. M. Sack and S. F. Besugly, Sowphys. **5**, 146 (1934).
[5] A. E. Brodskii and A. M. Sack, Acta Physicochem. (1935).
[6] P. Daure, Ann. d. Physik **12**, 375 (1929); S. Bhagavantam, Ind. J. Phys. **5**, 48 (1930) etc.
[7] The orientational calculation of H. Braune and G. Engelbrecht (Zeits. f. physik. Chemie **B19**, 303 (1932)) gives $\eta=3.5\times10^{-18}$, and from data for densities, refractive indices and dielectric constants (Landolt's Tables) it follows that $\eta=1.4\times10^{-18}$. A comparision with other chlorides and with compounds of As^{+++} indicates likewise a considerable moment of liquid $AsCl_3$.
[8] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt*, pp. 154, 215.
[9] Cf. below.
[10] B. Trumpy, Zeits. f. Physik **66**, 790 (1930); **68**, 675 (1931); Det. Kgl. Vid. Selsk. Forh. **4**, 102 (1931).
[11] Cf. the juxtaposition of D. A. Andrews and J. W. Murray, J. Chem. Phys. **2**, 630 (1934).
[12] D. M. Dennison, Phil. Mag. **1**, 195 (1926).

TABLE II.

	β	α	f	f'	$r:h$	$r:s$
Pure $AsCl_3$	63° 53′	102° 10′	1.70×10^5	0.73×10^5	3.54	1.56
$AsCl_3+CH_3OH$	64° 45′	103° 6′	1.52×10^5	0.73×10^5	3.67	1.57
$AsCl_3+C_2H_5OH$	63° 32′	101° 46′	1.47×10^5	0.73×10^5	3.48	1.55

NOTATION: β—the angle between the axis of symmetry of the pyramid and its edge, α—the angle between two bonds As−Cl, f—the elastic constant of the bond As−Cl, f'—the same for the bond Cl−Cl r—the distance Cl−Cl and s—the distance As−Cl in A.

This assignment gives for the molecule $AsCl_3$ the constants indicated in the first line of Table II. The resulting values for the constants of the elastic bonds f and f' and for the angle β between the edge As−Cl and the altitude of the pyramid satisfy well all the four Dennison equations. The inverse calculation gives for the frequencies:

436 [410], 150 [159], 387 [372] and 188 [195]

(in brackets are given the mean observed values from Table I). From the angle β we can readily find the ratio $r:h$ of the edge of the base (Cl−Cl) to the altitude, the ratio $r:s$ of the edge of the base to the edge As−Cl and the angle between the two edges As−Cl. These values are likewise given in Table II. The results obtained are in fairly good agreement with the data resulting from electron diffraction[13] which give:

$\alpha=101°$ [102°]; $\beta=63°$ [64°]; $r:s=1.54$ [1.56]

(in brackets are the results of our calculations). Thus, the conclusions about an inapplicability of Dennison's formulae to the computation of molecule $AsCl_3$[14] are dubious.

The old data of Bhagavantam[15] disagree equally both with ours and with the electronographic ones. In the recent paper of Howard and Wilson[16] a computation of the constants of the molecule $AsCl_3$ is made for central as well as valence forces. They obtained for the former model $f=1.80\times10^5$ and $f'=0.60\times10^5$ dyne/cm in tolerable agreement with our data but an inverse calculation of the frequencies gives a considerable deviation from experimental values.

In order to compute the moments of inertia of the molecule $AsCl_3$ one must know the distances r and s between Cl−Cl and As−Cl, which cannot be obtained from the Raman spectrum or electronographic data only. Assuming the radii of the ions As^{+++} and Cl^- to be 0.69 and 1.81A according to Goldschmidt and Pauling and ignoring their deformation, we find $r:s=1.45$ instead of 1.56 obtained by us. The agreement is sufficiently good; the distances As−Cl and Cl−Cl are to be identified with the sum of radii. Then for both moments of inertia about the symmetry axis and perpendicular to it, the values 765 and 565×10^{-40} will be obtained. Unfortunately the absence of rotational structure did not allow us to verify these values. The moments of inertia computed by us depend in a very strong way upon the errors in values of r—their accuracy is not high.

For the molecule $AsCl_3$ in its mixtures with alcohols the assumption was made that the pyramid remains regular. The ratio $\omega_1\omega_2/\omega_3\omega_4$ in spite of a considerable change in ω_1 and ω_3 remains nearly constant in mixtures which confirms a very small deformation of the molecule $AsCl_3$ from the dipoles of the alcohols. Actually, the geometrical constants of the pyramid almost do not change and neither does the constant f'. On the other hand the constant f decreases by 9–13 percent which indicates the weakness of the bond As−Cl. An analogous computation for $AsCl_3$ in benzene and carbon tetrachloride was not made, because in these cases the shifts from pure $AsCl_3$ are not outside the limits of possible errors of the values quoted in Table II.

The Raman lines of $AsCl_3$, in particular ω_3 and ω_4, are very diffuse in alcohols which is due, presumably, to the Stark-effect, caused by the dipoles of the alcohols. In C_6H_6 and CCl_4 this diffusion of the lines is only weakly manifested.

[13] L. O. Brockway and F. T. Wall, J. Am. Chem. Soc. **56**, 2373 (1934).

[14] Don M. Yost and J. E. Sherborne, J. Chem. Phys. **2**, 125 (1934) and Don M. Yost and T. F. Anderson, ibid. **2**, 624 (1934). These authors proceed from another assignment of frequencies by analogy with PCl_3 ($\omega_1=410, \omega_2=193, \omega_3=370, \omega_4=159$).

[15] Cf. Kohlrausch, ref. 8., p. 201 (assignment the same as it is by Yost).

[16] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934) (assignment the same as it is by Yost).

On the Electrolytic Separation of the Hydrogen Isotopes

O. HALPERN, *New York University*, AND PH. GROSS, *University of Vienna*

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Starting from the hypothesis that the rate-determining process in the electrolysis of gases is constituted by the recombination of the gas atoms on the electrode, a formula is developed which expresses the separation coefficient as a function of well-known thermodynamic constants of H and D compounds and of the frequencies with which the atoms carry out their thermal oscillations on the electrode. The formula gives a certain range for the value of the separation coefficient which is in good agreement with the observations. As a by-product of these calculations a relation is established between the normal electrode potentials of H and D.

I. INTRODUCTION

SINCE the discovery of the electrolytic separation of the two hydrogen isotopes a series of papers has been concerned with attempts to obtain theoretical explanations for the observed effects. A complete survey of the merits of the various theories can be found in the recently published report by Urey and Teal.[1] From it it is obvious that at present we cannot claim to possess a satisfactory theory of the phenomenon of electrolytic separation. It therefore will be attempted in the present paper to derive a theoretical expression for the separation coefficient, starting from assumptions as closely defined as possible and, as far as we know, nowhere in disagreement with experiment. In distinction from most of the theories we shall assume that the rate determining process in the electrolytic production of gases is constituted by the recombination of the gaseous atoms on the electrode.

In support of this hypothesis we can adduce the following very general experimental facts:

1. Overvoltage phenomena of a marked character seem to appear only at the electrolytic production of *gases*. We thereby, of course, discard all such cases of overvoltage in which, due to slow diffusion, an impoverishment of ions at the electrode occurs. Such cases are of no concern for the electrolytic separation of hydrogen where the ionic concentrations in the solution are invariably high. The fact that only gases show this marked retardation in the electrolytic process seems to us to indicate very strongly that it is the recombination process which determines the rate of electrolysis for a given voltage.

2. The separation coefficient seems to be the same whether the electrolysis is carried out in acid or alkaline solutions. This second point seems to us to speak in disfavor of theories which attempt to ascribe the separation to a difference in the rate of *discharge* of the two kinds of hydrogen ions. In strongly acid solutions it is plausible that the discharge at the electrode is carried out by the H ions and a theory establishing a difference in the speed of discharge for the two ions could perhaps account for the observed phenomena. On the other hand, due to the smallness of the dissociation constant of water, there are no hydrogen ions present in the neighborhood of the electrode for all alkaline solutions used in the experiments. In alkaline solutions therefore, differences in the speed of discharge of the hydrogen ions would be without any importance and could not explain the observed separation.

Keeping these two facts in mind we assume that the "slow process" is determined by the recombination at the electrode while the discharge of the ions and the establishment of the equilibrium between the solution and the electrode shall be considered to be "instantaneous" processes. We do not feel certain that the diffusion between electrode and solution is always sufficiently fast, but it is probably a fair assumption to treat the process as instantaneous for not too large current densities. On the other hand, the current densities should not be taken too small because the back diffusion from the gas to the electrode would then have to be taken into account. For the following we assume these conditions to be satisfied; particularly as

[1] H. C. Urey and G. K. Teal, Rev. Mod. Phys. **7**, 34 (1935). Cf. particularly pp. 41–48.

far as the back diffusion of the gas is concerned, these assumptions are probably well justified.

The paper is divided into the following sections: In paragraph II we briefly review a few thermodynamic formulae and approximations which are generally used for this type of calculations. Paragraph III contains the derivation of a relation between the normal electrode potentials for H and D. This relation is derived in a rather devious manner for the sake of an extension of the method in paragraph IV which is essential for the treatment of the nonequilibrium case of electrolysis. There, on the basis of the physical factors outlined in the introduction, we derive and discuss the theoretical explanation for the separation coefficient.

II. Several Thermodynamic Relations

In the following calculations the solution of electrolytes (which themselves might contain hydrogen) in mixtures of heavy and light water will be treated thermodynamically as ideal solutions. Concentration symbols c, referring to the solution, the electrode and the gas phase, will as far as necessary be distinguished by an upper s, e, g. The *ratio* of the analytic concentration of light to heavy hydrogen in the solution and in the gas phase will be denoted by a^s and a^g respectively. Neglecting the hydrogen content of the electrolyte and the amount of free atoms of hydrogen in the gas phase, we have for a^s and a^g the following relations:

$$a_g=(2c_{H_2}{}^g+c_{HD}{}^g)/(c_{HD}{}^g+2c_{D_2}{}^g), \tag{1a}$$

$$a_s=(2c_{H_2O}{}^s+c_{HDO}{}^s)/(c_{HDO}{}^s+2c_{D_2O}{}^s). \tag{1b}$$

In the gaseous as well as in the liquid phase there exist equilibrium conditions for the different kinds of molecules containing the two hydrogens. For the following we need the relations given below

$$c_H{}^{g2}/c_{H_2}{}^g=K_{11}, \tag{2a}$$

$$c_H{}^g c_D{}^g/c_{HD}{}^g=K_{12}, \tag{2b}$$

$$c_D{}^{g2}/c_{D_2}{}^g=K_{22}, \tag{2c}$$

$$c_H{}^+ c_{OH}{}^-/c_{H_2O}{}^s=L_{11}, \tag{3a}$$

$$c_H{}^+ c_{OD}{}^-/c_{HDO}{}^s=L_{12}, \tag{3b}$$

$$c_D{}^+ c_{OH}{}^-/c_{HDO}{}^s=L_{21}, \tag{3c}$$

$$c_D{}^+ c_{OD}{}^-/c_{D_2O}{}^s=L_{22}. \tag{3d}$$

From general statistical considerations which are in fairly good agreement with experiment we assume the following relations between the various equilibrium constants to hold true:

$$K_{11}K_{22}/K_{12}{}^2=L_{11}L_{22}/L_{12}\cdot L_{21}=4. \tag{4}$$

This procedure has been adopted by most writers[1] in this field and we consider the reasons justifying these assumptions to be satisfactory. Combining the dissociation Eqs. (2) and (3) with the relations (1) and (4) we obtain the following equations:

$$c_H{}^+/c_D{}^+=(L_{11}/2L_{12})a^s, \tag{5a}$$

$$c_H{}^g/c_D{}^g=(K_{11}/2K_{12})a^g, \tag{5b}$$

$$a^g/a^s=K_F. \tag{5c}$$

The (equilibrium) value of K_F has been experimentally determined. The latest determination made by A. and L. Farkas[2] led to $K_F\sim 3$.

III. Normal Electrode Potentials of H and D

Consider an electrolytic solution of heavy and light water in *equilibrium* with the gas phase. This gas phase will also contain (unobservably small) quantities of H and D atoms. Into the solution is dipping an electrode containing H and D atoms. The nature of the electrode is indifferent to the equilibrium. We shall now formulate thermodynamic conditions for the equilibrium of the whole system.

The electric potential difference between the electrode and the solution can be expressed in two different ways

$$\Delta_H=E_{0H}+\frac{RT}{F}\log\frac{c_H{}^+}{c_H{}^e/c_{H0}{}^e}, \tag{6a}$$

$$\Delta_D=E_{0D}+\frac{RT}{F}\log\frac{c_D{}^+}{c_D{}^e/c_{D0}{}^e}. \tag{6b}$$

$c_{H0}{}^e$ and $c_{D0}{}^e$ denote the concentration of H and

[2] A. Farkas and L. Farkas, J. Chem. Phys. **2**, 468 (1934).

D atoms on the electrode in equilibrium with H_2 or D_2 at the pressure of 1 atom. Since, for electrostatic reasons $\Delta_H = \Delta_D$ we obtain by subtracting (6b) from (6a) the relation

$$E_{0H} - E_{0D} = -\frac{RT}{F} \log \frac{c_D^e}{c_H^e} \frac{c_H^+}{c_D^+} \frac{c_{H0}^e}{c_{D0}^e}. \quad (7)$$

We now express c_H^e and c_D^e through the concentrations in the gas phase.

$$c_H^e = k_H c_H^g, \quad (8a) \qquad c_D^e = k_D c_D^g. \quad (8b)$$

k_H and k_D denote the distribution coefficients of the atoms between electrode and gas phase. Analogously

$$c_{H0}^e = k_H c_{H0}^g = k_H K_{11}^{\frac{1}{2}} (c_{H_2}^g)_0, \quad (9a)$$

$$c_{D0}^e = k_D c_{D0}^g = k_D K_{22}^{\frac{1}{2}} (c_{D_2}^g)_0. \quad (9b)$$

Using (8) and (9) and inserting (5a) to (5c) into (7) we obtain

$$E_{0H} - E_{0D} = -\frac{RT}{F} \log a_s \frac{(c_{D_2}^g)_0}{(c_{H_2}^g)_0} \frac{1}{a^g} \frac{L_{11}}{2L_{21}}. \quad (10)$$

Since by definition $(c_{H_2}^g)_0 = (c_{D_2}^g)_0$ we finally arrive at the following formula for the difference of the normal electrode potentials of H and D:

$$F_{0H} - E_{0D} = -(RT/F) \log (L_{11}/2L_{21})(a^s/a_g)$$
$$= -(RT/F) \log (2L_{12}/L_{22})(1/K_F). \quad (11)$$

The difference between E_{0H} and E_{0D} is according to (11) very small. Though we do not have very exact determinations of $L_{11}/2L_{21}$ it has been estimated that its value lies around 3. This leads, with the value given above for K_F, to a value for $E_{0H} - E_{0D}$ which is very small.

IV. Determination of the Separation Coefficient

For the case of a current flowing the formulae of paragraph III need modification only as far as the connection between c^e and c^g is concerned while the relations between the potentials Δ and c^s, c^e remain intact according to the hypothesis explained in paragraph I. We therefore obtain here again the relations, (6a), (6b) and by subtracting,

$$0 = E_{0H} - E_{0D} + \frac{RT}{F} \log \frac{c_H^+}{c_D^+} \frac{c_D^e}{c_H^e} \frac{c_{H0}^e}{c_{D0}^e} \quad (7)$$

$$= E_{0H} - E_{0D} + \frac{RT}{F} \log \frac{L_{11}}{2L_{21}} a^s \frac{c_D^e}{c_H^e} \frac{k_H}{k_D} \frac{L_{11}}{2L_{12}}. \quad (7a)$$

Making use of (11) and (4) we can write (7a) in the form

$$c_H^e / c_D^e = (k_H/k_D)(K_{11}/K_{22})^{\frac{1}{2}} K_F a^s. \quad (12)$$

The other terms in (7a) cancel each other.

To determine with the help of (12) the amount of H_2 and D_2 given off irreversibly to the gas phase we have to make an hypothesis concerning the mechanism of recombination. It seems reasonable to consider this process a bimolecular reaction. We so obtain for $[H_2]/[D_2]$ the expression

$$[H_2]/[D_2] = a^g$$
$$= (2\lambda_{11} c_H{}^{e2} + \lambda_{12} c_H{}^e c_D{}^e)/(\lambda_{12} c_H{}^e c_D{}^e + 2\lambda_{22} c_D{}^{e2}). \quad (13)$$

In this expression the quantities λ_{ik} are the velocity constants of the corresponding reactions. Following the assumptions made in paragraph II (cf. (4)) we correspondingly have for the ratio of the λ_{ik} the relation[1]

$$\lambda_{11}\lambda_{22}/\lambda_{12}{}^2 = 1/4. \quad (14)$$

Thereby (13) reduces to $(\lambda_{11}/\lambda_{22})^{\frac{1}{2}}(c_H{}^e/c_D{}^e)$. The separation factor α is defined by the relation

$$\alpha = a^g/a^s.$$

From (12), (13), (14) we finally obtain for α the equation

$$\alpha = (k_H/k_D)(\lambda_{11}/\lambda_{22})^{\frac{1}{2}}(K_{11}/K_{22})^{\frac{1}{2}} K_F. \quad (15)$$

This theoretical expression for (15) now has to be discussed.

For the physical interpretation of (15) two kinds of factors have to be distinguished: K_F has been calculated to be about 3.0 and has been experimentally determined as well (cf. paragraph II (5c)). $(K_{11}/K_{22})^{\frac{1}{2}}$ though not directly empirically determined, can be easily calculated from other thermal or spectroscopical measurements. Its value at room temperature has been calculated[3] from the results of Johnston and

[3] We are indebted to Dr. G. M. Murphy for this calculation.

Long[4] and of Giauque.[5] This gives the value

$$K_{11}/K_{22}=14. \tag{16}$$

The other factors in (15) are not as fully determined as the two already discussed. For the ratio of the distribution coefficients of H and D atoms k_H/k_D we have from general statistical arguments the relation

$$\frac{k_H}{k_D}=2^{\frac{1}{2}}e^{-3hV_H(1-1/\sqrt{2})/2kT}\frac{(1-e^{-hV_H/\sqrt{2}kT})^3}{(1-e^{-hV_H/kT})^3}. \tag{17}$$

(V_H=frequency of oscillation of the H atom on the electrode.) (17) is nothing but the ratio of the vapor pressure equations for the two atoms; in it, it has been assumed that the three frequencies of oscillations of the atom on the metal surface are equal to each other, and that, of course, the "heat of vaporization" for the two isotopes from the hypothetical vibrationless state shall be the same. The exponential factor in (17) is, due to the difference in zero-point energy of the oscillating atoms on the electrode.

The ratio of the velocity constants, $(\lambda_{11}/\lambda_{22})^{\frac{1}{2}}$, now can be easily calculated, assuming the activation energy Q of the process of recombination to be the same for H and D (except for the difference in zero-point energy). Writing for Q the expression $a=N_1hV_H=N_2hV_D=N_2hV_H/\sqrt{2}$ wherein N_1 and N_2 are assumed to be large compared to 1, one can easily derive for $(\lambda_{11}/\lambda_{22})^{\frac{1}{2}}$ the relation

$$(\lambda_{11}/\lambda_{22})^{\frac{1}{2}}=e^{+3hV_H(1-1_H/\sqrt{2})/2kT}\times\left(\frac{N_1}{N_2}\right)^{(f-1)/2}\left(\frac{1-e^{-hV_H/kT}}{1-e^{-hV_H/\sqrt{2}kT}}\right)^{(f-1)/2}. \tag{18}$$

In this relation the exponential factor is due to the zero-point energy while the factor $(N_1/N_2)^{(f-1)/2}$ arises from the different number of states which lead to an energy equal to, or larger than, the activation energy. In (18) f stands for the number of degrees of freedom of the particles entering into the reaction; in our case f is equal to 6.

We shall here give the derivation of (18) for a system of two degrees of freedom, a generalization is then very simple. The probability that an oscillator system of two degrees of freedom with a frequency V has an energy equal to or larger than the activation energy $Q=NhV(\gg kT)$ is given by the sum of the probabilities of the following mutually exclusive conditions. (We denote in the following the energy of the first degree of freedom with ϵ_1 that of the second degree of freedom correspondingly with ϵ_2.)

$$\left.\begin{aligned}
&(1)\,\epsilon_1=0, \quad \epsilon_2\geqq NhV, \quad p_1=e^{-Q/kT}(1-e^{-hV/kT}),\\
&(2)\,\epsilon_1=hV, \quad \epsilon_2\geqq(N-1)hV, \quad p_2=e^{-Q/kT}(1-e^{-hV/kT}),\\
&\vdots\\
&(N+1)\,\epsilon_1\geqq Q_1, \quad \epsilon_2\geqq 0, \quad p_{N+1}=e^{-Q/kT},
\end{aligned}\right\} \tag{19}$$

$$P=\sum_i pi. \tag{20}$$

Since there are altogether $N+1\sim N$ different cases each with the probability $e^{-Q/kT}(1-e^{-hV/kT})$ the relation (20) takes on account of (19) the form

$$P=(Q/hV)e^{-Q/kT}(1-e^{-hV/kT}), \tag{21}$$

from which (18) can be easily deduced. The final theoretical expression therefore for the separation coefficient α takes the form

$$\alpha=(K_{11}/K_{22})^{\frac{1}{2}}K_F 2^{\frac{1}{2}}\left(\frac{1-e^{-hV_H/kT}}{1-e^{-hV_H/\sqrt{2}kT}}\right)^{\frac{1}{2}}. \tag{22}$$

The numerical value of this expression therefore depends apart from known constant on the ratio hV_H/kT.

It is of interest to compare two limiting cases, (a) $hV_H/kT<<1$. After expanding the exponentials (22) takes the form

[4] H. L. Johnston and E. A. Long, J. Chem. Phys. **2**, 389 (1934).
[5] W. F. Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

$$\alpha=(K_{11}/K_{22})^{\frac{1}{2}}K_F\sim 11.$$

This case corresponds physically to atoms lightly bound to the electrode (the thermal energy of the oscillators has equipartition value). (b) $(hV_H/kT)>>1$. This corresponds to very tightly bound atoms (large oscillatory frequency). The thermal energy of oscillation is very low. In this case (22) takes the form

$$\alpha=(K_{11}/K_{22})^{\frac{1}{2}}K_F 1.19,$$

with a numerical value $\alpha\sim 13$. We should therefore theoretically expect the separation coefficient to lie somewhere between the two limits.

The difference of the electrode-material according to the factors presented enters only through the difference in the oscillation frequency of the atoms bound to the metal. It seems important to emphasize that the zero-point energy of the atoms bound to the metal surface does not enter into the expression for the separation coefficient. This is due to the fact, as ascertained from (17) and (18), that the zero-point enters twice, namely, into k_H/k_D and $(\lambda_{11}/\lambda_{22})^{\frac{1}{2}}$ and with opposite sign in the exponentials of the two terms.

The values theoretically obtained seem to be in good agreement with experiments. Brown and Daggett[6] find that the fractionation factor is about 12 in the case of iron electrodes. McLaren[7] finds that this factor depends on the surface and on the current density.

With increasing temperature the coefficient of separation should decrease because the quantities K_{11}/K_{22} and K_F have negative temperature coefficient and the ratio hV/hT decreases. All these effects tend to diminish the separation factor. We do not know of any experiments so far made which would allow a definite check on the theory in this respect, though observations reported by Urey and Teal[8] seem to be in agreement with this prediction.

One of the authors (O. H.) has had the pleasure of privately discussing the problem treated in this paper with Professor H. C. Urey.

[6] W. G. Brown and A. F. Daggett, J. Chem. Phys. **3**, 216 (1935).
[7] J. McLaren, Private communication.
[8] Reference 1, p. 43.

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On the Dissociation Constants of Acids in Light and Heavy Water

O. HALPERN, *New York University, University Heights*
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The ratio of dissociation constants of acids in light and heavy water is shown to become the larger the weaker the acid. This is a consequence of the differences in zero-point energy of the proton (deuteron) when attached to the anion or the neutral water molecule.

DIFFERENCES in the dissociation constant of acids when dissolved in light and heavy water have been observed rather early. These differences are of importance not only for conductivity measurements but even to a higher extent for reaction problems and catalysis phenomena in which hydrated protons and deuterons are involved. Since particularly the formation of the activated state often depends on the acceptance of the proton (deuteron) the difference in the dissociation constants for the two ions becomes of considerable importance. In the following we present a simple relation which will allow us to predict qualitatively how this difference depends on the nature of the acid.

We discuss the dissociation of an acid in a dilute aqueous solution. The ratio K_H/K_D, where K_H and K_D stand for the dissociation constant of HA and DA, respectively, now depends mainly on the relative magnitude of the binding forces acting on the ions when attached to the anion A or to the neutral water molecule (dissociated, hydrated state). We introduce the assumption which can be proved for many cases and very probably is generally true, that the frequency of oscillation of the ions in either state

increases with increasing *binding energy*. It is obvious that it increases with increasing *force*, but only in very special cases, could we imagine that field of force and binding energy do not go parallel.

Now, according to thermodynamics, the ratio K_H/K_D becomes equal to

$$\frac{K_H}{K_D}=\exp -\frac{fh(V_H{}^w-V_H{}^A-V_D{}^w+V_D{}^A)}{2kT}, \quad (1)$$

f=number of degrees of freedom of oscillation.

In (1), $V_H{}^A$ stands for the frequency of oscillation of the proton attached to the anion $V_H{}^w$ for the frequency of oscillation of the proton when attached to the neutral water molecule, and correspondingly for the deuteron. About the relative magnitudes of $V_H{}^w$ and $V_H{}^A$ we can now say that, according to our hypothesis

$$V_H{}^w<V_H{}^A \quad (2)$$

except, perhaps, for the case of some extremely strong acids. This can be seen easily in the following way: Every proton has, statistically speaking, a certain number of places where it can attach itself, namely, N_w neutral water molecules and N_A anions. Since $N_w \gg N_A$ all acids should be completely dissociated if no energetic factors would enter, or, in other words, if the binding energy to the anion would not very much exceed the binding energy to the water molecule (energy of hydration). Therefore $V^w<V^A$ and since

$$V_H=\sqrt{2}\,V_D$$

we obtain for the ratio K_H/K_D

$$\frac{K_H}{K_D}=\exp -\frac{fh(1-1/\sqrt{2})(V_H{}^w-V_H{}^A)}{2kT}>1. \quad (3)$$

Now the difference between $V_H{}^A$ and $V_H{}^w$ becomes the larger the weaker the acid, i.e., the more the binding energy of the anion exceeds the energy of hydration. This leads to the result given in the summary that *the ratio* K_H/K_D *increases the weaker the acid becomes.*

As one of the weakest acids we might consider water itself. The ratio K_{H_2O}/K_{D_2O} in this case therefore should be expected to exceed the ratio of all acids which show stronger dissociation than water itself does.

If, in a chemical reaction the rate is determined by a critical complex C formed through the addition of a proton (deuteron) to some other molecule, the arguments of this paper allow a prediction as to whether the reaction in light or heavy water will be faster. For this purpose consider the critical complex C as an "acid" being able to dissociate according to the scheme

$$H_2O+C_H \rightleftarrows M+H_3{}^+O,$$

$$D_2O+C_D \rightleftarrows M+D_3O.$$

If the binding energy of the proton to M is larger than its energy of hydration, then the complex might be considered a "weak acid," and the dissociation constant of the complex will be larger for light than for heavy water, its concentration therefore, smaller, and the reaction velocity smaller in light than in heavy water. Conversely, if the binding energy of M for protons is smaller than the hydration energy the complex becomes a "strong acid." The "dissociation of the complex" is larger for heavy than for light water because the zero-point energy of $H_3{}^+O$ is larger than that of C. The reaction velocity therefore is smaller in heavy than it is in light water.

It becomes apparent that no general rule exists about the relative rates of ionic reactions in heavy and light water but that everything depends on the binding energy of H^+ in the critical complex.

The author understands that Ph. Gross in Vienna and his collaborators are going to present experimental material in support of the view formulated above.

The Theory of Galvanic Potentials. I

PH. GROSS, *University of Vienna*, AND O. HALPERN, *New York University*

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In this paper a thermodynamic study of the theory of galvanic electrode potentials is presented. It is shown that, starting from strictly equilibrium conditions, the series of normal electrode potentials can be expressed through other partly known thermodynamic quantities, one group of which refers to the solid phase only, independent of the solvent used, while the other is characterized by the type of solvent.

I. INTRODUCTION

THERE exists a large literature on the theory of galvanic potential series and in particular on their suspected connection with the voltaic series. Among the papers most important in this connection we only want to point out the investigation by K. F. Herzfeld,[1] who succeeded in deriving thermodynamic relations between normal electrode potentials and other thermal quantities like heat of solution, etc. Though, from this, as well as from other investigations, it was apparent that the problem possesses an intrinsic complexity, still century old attempts are being revived again and again for the purpose of showing that the galvanic and the voltaic series are essentially equivalent. Though all these attempts are theoretically unsound, as will become even more apparent from the following, it could be said for their justification that the order of the metals in both series shows a certain amount of parallelism, a fact that encouraged the construction of theories which aim to derive this parallelism from general principles.

In the present paper we shall give a thermodynamic derivation for the differences in normal electrode potentials. (It is, of course, the difference only which can be brought in connection with observable thermodynamic quantities). From formula (6) of paragraph II it will become apparent that the differences in the normal electrode potentials can be expressed essentially by the differences in two groups of quantities; the first group of these quantities refers only to the properties of the substances forming the electrode, containing quantities like the heat of vaporization of the neutral electrode atom, and the ionization energy of the metallic atom in the gaseous phase, or on the Richardson constants for the electrons or positive ions which can be emitted from the electrode. The second group refers to the free energy which becomes liberated when a *gaseous* ion of the substance forming the electrode becomes dissolved in the solvent. While the first group of quantities is completely independent of the nature of the solvent used, the second group does not depend on the structure of the metal electrode itself.

II. THERMODYNAMIC EXPRESSIONS FOR GALVANIC ELECTRODE POTENTIALS

We consider an electrolytic solution containing two different univalent cations and a common anion. Two electrodes are dipping into this electrolytic solution; they consist respectively of the metals 1 and 2, which form the cations present in the solution.

The solution and the metals shall be considered to be in thermodynamic equilibrium with the gas phase present above the solution, this gas phase containing all neutral and charged particles as given by the equilibrium relations of thermodynamics.

The restrictions as to the valency of the cations present, the common anion, etc., are only made to give the following formulae the simplest form and do not diminish the generality of the considerations.

In general the solution and the gas phase will not be in equilibrium. It is *this fact* which produces the electromotive force of the element just described. To obtain equilibrium it is necessary that the two cations in the solution be present in a ratio which can be determined from the following simple consideration: In equi-

[1] Herzfeld, Ann. d. Physik **51**, 257 (1917).

librium the work done by carrying a unit charge from one electrode to the other must be independent of the path chosen. The work done in carrying a charge from the electrode 1 to the electrode 2 through the solution is given by the expression:

$$G_{12}=\Delta_{10}-\Delta_{20}+(RT/F)\log(c_1^s/c_2^s),$$

in which Δ_{10} stands for the potential difference between the metal and the solution at the concentration (1) of its ion and c_1, c_2 denote, respectively, the concentration of the cations 1 and 2. We should more correctly take the activity of the ions but this difference can be neglected for our purposes. Carrying the same charge through the gas phase, the work done would be equal to V_{12}, the Volta potential difference between the metals 1 and 2. The equation

$$\Delta_{10}-\Delta_{20}-V_{12}=(RT/F)\log(c_2^s/c_1^s) \quad (1)$$

gives us the conditions of equilibrium. The right-hand side of (1) equals the difference of the normal electrode potentials of the metals 1 and 2.

We now express c_1^s and c_2^s through the concentrations of the ions and atoms in the gas phase, which in turn are determined by the ionization equilibria of the gas atoms and the vapor pressures of the metals. We thus have the following relations:

$$\frac{c_2^s}{c_1^s}=\frac{c_2^{+g}}{c_1^{+g}}e^{-(W_2-W_1)/RT}=\frac{c_2^{+g}}{c_1^{+g}}e^{-[(W_2'-W_1')F]/RT}. \quad (2)$$

Here W_1 and W_2 stand for the difference in free energy of the ions 1 and 2 in the liquid and in the gas phase. This difference in free energy consists of two parts: (possibly) of a surface potential difference $F\phi$ between the liquid and the gaseous phase and of the work FW' gained or lost by transferring the ion from the vacuum into the liquid. This work is due to the interaction between the ion and molecules of the solvent. In conformity with general thermodynamic principles, the first part drops out of the formula.

c_1^{+g} and c_2^{+g} are, respectively, determined by their ionization equilibria

$$c_1^{+g}c_e/c_1^g=e^{-I_1F/RT}f(T), \quad (3a)$$

$$c_2^{+g}c_e/c_2^g=e^{-I_2F/RT}f(T). \quad (3b)$$

$f(T)$ denotes the phase-volume of the electron. In (3a) (3b), I_1F and I_2F stand for the ionization energy of the atoms. We here neglect excited electronic levels of the atoms which lie far too high to be of any importance for the problem under consideration. Finally, since the electron concentration c_e is common to both ionization equilibria, we can determine the ion concentrations in the gas phase by making use of the vapor-pressure equation and thus describe everything by properties of the solid phase. We obtain the relation

$$c_1^g/c_2^g=(A_1/A_2)e^{-(Q_1-Q_2)F/RT}. \quad (4)$$

A_1, A_2 are known constants, QF denotes the heat of vaporization at absolute zero. Connecting now Eqs. (2), (3) and (4) we can express c_2^s/c_1^s in the form

$$c_2^s/c_1^s=(A_2/A_1)e^{-F(W_2'-W_1'+I_2-I_1+Q_2-Q_1)/RT}. \quad (5)^2$$

We insert (5) into the equilibrium condition (1) which contains the difference of normal electrode potentials and so finally obtain for them the following relations:

$$E_{01}-E_{02}=(RT/F)\log(A_2/A_1)+(I_1-I_2)+(a_1-a_2)+(W_1'-W_2'). \quad (6)$$

The first term in (6) is in all practical cases very small and can be neglected.

(6) contains the formal justification for the statements made in the introduction. We first of all notice that the surface potential of the liquid has dropped out since it is the same for both cations. The first three terms (on the right side of (6)) refer to properties of the *electrode material only*. We can express the sum of the ionization potential and the heat of vaporization with the help of two other quantities, namely, the Richardson constants b for the electrons and positive ions which determine the work necessary to remove either of these two particles from the metal to the gas phase at absolute zero. From the first law of thermodynamics it is obvious that the relation

$$Q+I=b_+ +b_- \quad (7)$$

must hold. This relation mainly expresses the fact that we can produce an ionized atom in the gas phase at absolute zero with the same amount

[2] Similar considerations have been used in a paper by T. J. Webb, J. Am. Chem. Soc. **48**, 2589 (1926).

of energy either by evaporating a neutral atom and then ionizing it or by evaporating the charged components. If $W_1' - W_2'$ would be zero, then the galvanic potential difference would still not be given by the voltaic potential difference between the two metals, which is equal to the difference between the *Richardson constants for the electrons alone*, since the difference between the values of the Richardson constants for the positive ions has to be added, which in general is of the same order of magnitude. Still a certain parallelism between the voltaic and galvanic potentials could then be expected because the Richardson constants for the positively and negatively charged particles go somewhat parallel to each other.

Now the difference between the Richardson constants, being of the order of magnitude of 1 volt, cannot in general be considered to be large compared to the difference in the work done by immersing a charged ion into a liquid. The simple electrostatic considerations: work done by a sphere of radius a when transferred from a medium with the dielectric constant 1 to another with the dielectric constant D leads to values for $W_1' - W_2'$ which are of the same order of magnitude as the other terms in (6). There does not therefore exist any general theoretical principle which would justify the much discussed hypothesis of equivalence of voltaic and galvanic potentials. In a subsequent communication the authors intend to present what evidence can be derived from a study of ionic diameters and correlated quantities as to the magnitude of the work done by transferring ions from the gaseous into the liquid phase.

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Rotating Polar Groups in "Organic" Molecules

WILLIAM ALTAR, *The Pennsylvania State College*

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The temperature dependence of the electric moment, observed in the case of molecules with rotating polar groups, permits a quantitative explanation in terms of intra-molecular forces opposing free rotation of the groups. Specifically, the following questions have been raised and treated: I. The statistical weight to be associated with a configuration. II. Approximation of the periodic potential function by its first and second Fourier component. III. An application to 1,2-dichloroethane is given and a plausible potential of interaction between the two CH_2Cl groups is obtained. The result suggests the presence of repulsive forces between two bound chlorine atoms at distances as large as 4.0 Angstrom. IV. The related question of the thermal equilibrium ratio of the *cis* and *trans* isomers of dichloroethylene is discussed. A new explanation of the observed value is proposed, which attributes about equal heat of formation to both isomeric forms.

INTRODUCTION: STATEMENT OF THE PROBLEM

IT is now generally recognized that the deviations of the molar polarization *vs.* T^{-1} curves from a straight Debye line, as are observed with 1,2-dichloroethane, diacetyl, and similar molecules,[1] must be attributed to the presence of forces restricting free rotation of the polar groups around the single C–C bond,[2, 3] and that from the temperature variation of the dipole moment we can gather information with regard to these forces.[4, 5, 6] This information is important and, indeed, unique because in this particular phenomenon—unlike others where interatomic forces manifest themselves (second virial coefficient, friction in gases)—the groups approach each other under rigidly defined geometrical conditions which can be derived with great accuracy from x-ray and electron diffraction data.

[1] C. T. Zahn, Phys. Rev. **38**, 521 (1931); **40**, 291 (1932).
[2] L. Meyer. Zeits f. physik. Chemie **B8**, 27 (1930).
[3] Smyth, Dornte and Wilson, J. Am. Chem. Soc. **53**, 4242 (1931).
[4] Lennard-Jones and Pike, Trans. Faraday Soc. **30**, 830 (1934).
[5] Mizushima and Higasi, Proc. Imp. Acad. Japan **8**, 482 (1932).
[5a] Mizushima, Morino and Higasi, Physik. Zeits. **35**, 905 (1934).
[6] C. T. Zahn, Trans. Faraday Soc. **30**, 804 (1934).

As a refinement of the conceptions of free and restricted rotation, a distinction must be made with regard to the origin of the restricting forces.[7] In molecules like dichloroethane, the groups move under no restriction other than the one resulting from their own interaction. The single C−C bond in itself gives no preference to any internal configuration. Molecules like ethylene represent the other extreme where practically complete inhibition of the internal motion is enforced by the presence of a double bond. The conception of quantum resonance has presented us with the possibility of an intermediate case of which diphenyl is perhaps representative. The shortening of the linkage between the two rings[8] and other arguments have led L. Pauling and his co-workers to suggest that, with the single bond character prevalent, there might be resonance with double bond structures of comparable energy. Thus the idea of a hybrid bond with features borrowed from the parent structures might offer a more adequate description.[9, 10] If so, one should expect a stiffening of the single bond, a possibility which—if established from dipole data of o,o'-dichloro-diphenyl, let us say—might constitute an experimental test of "whether the phenomenon of resonance exists to anything like the imagined extent"[11] and whether it is present in that particular structure. In order to be quantitative, such a test would have to cover a wide temperature range. However, on account of the high boiling point of the compound, one must either improve the sensitivity of the dielectric measurements and adapt them to low vapor pressures, or else resort to the molecular beam method with its theoretical complications.

The applicability of the method is not restricted to the interaction between groups. A study of electric fields in crystals may, for instance, be based on the observed temperature dependence of the polarization in cases where polar groups are rotating in such fields.

It is the intention of this paper further to develop the analytic tool for such studies. As a test case, the general results are applied to the dipole data available for 1,2-dichloroethane, where we believe we have a fair understanding of the controlling factors, and where more dependable vapor measurements over a wider temperature range are at hand than for other compounds relevant in this connection. This will perhaps justify the extensive and somewhat laborious treatment given this molecule in section III.

Mathematically, the problem is to determine the potential function $V(\varphi)$ from a knowledge of the temperature variation of the mean square of the dipole moment. This, as will be shown below, amounts to solve for $V(\varphi)$ from a given equation:

$$\overline{\cos\varphi} = \int_0^{2\pi} d\varphi \cos\varphi e^{-V(\varphi)/kT} / \int_0^{2\pi} d\varphi e^{-V(\varphi)/kT}.$$

It is plausible that this could be done provided the left side of the equation were known for the entire temperature range. In view of the inherent experimental limitations, however, the best that can be done is to set up plausible potential functions which, upon proper choice of one or more disposable parameters, will best account for the experimental data over the accessible temperature range.

Previous investigators have taken a cosine function

$$V = V_1 \cos\varphi \qquad (1)$$

as the presumable expression for the potential energy. While this potential is suggested by the calculated mutual potential of the electric dipoles,[12] it is hardly one to do full justice to the complexity of the forces involved. The cosine shape of the electrostatic potential as calculated by Smyth, Dornte and Wilson[12] and given in a later part (curve C in Fig. 5), is enhanced if a flattening of the potential hill takes place as a result of a weakening of the bond moments by mutual induction. On the other hand, we shall find that electrostatic forces do not play a dominating part in dichloroethane, and that—

[7] E. Hueckel, Zeits. f. Physik **60**, 423 (1930).

[8] As N. V. Sidgwick remarks, a similar shortening has been observed with tetramethylbenzene in the link between the ring carbon and the methyl carbon, where resonance is obviously not a factor (See: discussion remark, Trans. Faraday Soc. **30**, 824 (1934)).

[9] Pauling and Sherman, J. Chem. Phys. **1**, 606, 680 (1933). For fuller references consult reference 10.

[10] Sutton, Trans. Faraday Soc. **30**, 789 (1934).

[11] Such doubts have been expressed with strong arguments by Bayley, Trans. Faraday Soc. **30**, 828 (1934).

[12] Smyth, Dornte and Wilson, J. Am. Chem. Soc. **53**, 4242 (1931).

except in a region which at moderate temperatures is effectively barred by forces of non-electrostatic origin,—their contribution stays within a few hundred calories/mole. The dominating forces arise in all probability from van der Waals attraction and from steric repulsion, and their potential remains yet to be calculated.

Considering, then, (1) as a first approximation suggested by the periodic character of the potential, we shall try the following as a second approximation:

$$V = V_1 \cos \varphi + V_2 \cos 2\varphi \qquad (2)$$

and shall derive the temperature dependence of the molar polarization resulting from (2). Since the more general assumption (2) puts two parameters at our disposal, we may expect a better agreement between theory and experiment, and more information than could be had on the basis of (1).

Before this derivation is given in section II, a point will be discussed in section I which has seemingly been neglected in past treatments. This concerns the statistical method of taking mean values of an assembly of systems possessing internal degrees of freedom.

I. The Statistical Weight of a Configuration

The formula for the statistical mean value of a quantity μ, averaged over an assembly of mechanical systems $\mathfrak{S}$ which move according to the laws of classical mechanics, calls for integration over the phase space of $\mathfrak{S}$:

$$\bar{\mu} = \frac{\int dq_1 \cdots dq_n \int dp_1 \cdots dp_n \mu e^{-H(pq)/kT}}{\int dq_1 \cdots dq_n \int dp_1 \cdots dp_n e^{-H(pq)/kT}}. \qquad (3)$$

In the case of rigid molecules, identical momentum integrals can be factored off both the denominator and the numerator so that integrations over configuration space only are required. When dealing with a molecule with internal degrees of freedom, the conventional omission of the integration in momentum space is no longer permissible. This point deserves attention with respect to the choice of the internal position variables, since it is the integration over their conjugate momenta which makes the values of the integrals in (3) independent of the particular choice of variables. Equally important, though, perhaps, less obviously so, is the integration over the three "external" momentum variables, since, in general, the three moments of inertia of the molecule do not remain constant, but vary with the internal configuration.

It is perhaps not superfluous, in view of different uses of the terms in recent discussions,[13] to set down at this point the proposed way of distinguishing between external and internal motion. Kinematically, such division can be effected in a variety of ways. Uniqueness is attained if we require that external and internal degrees of freedom be separable from each other in the sense that no cross-terms between the two sets of variables occur in the Hamiltonian form of the kinetic energy. With this end in view we define a rigid, rectangular frame X^i, attached to, and moving with, the molecule in a manner such that at any time the following expression vanishes:

$$\sum_i m_i [r_i \times v_i] = 0. \qquad (4)$$

Here, v_i is the velocity of the i'th particle relative to the moving frame and represents the part of the total motion referred to as internal. The remaining, external part is the motion $[r_i \times \omega]$ executed by the particle if it were rigidly attached to, and moving with the frame in its instantaneous relative position. Once given, the system X_i is determined at subsequent times by the equations:

$$dX_i/dt = [\omega \times X_i].$$

By ignoring translational degrees of freedom, the kinetic energy:

$$K = \tfrac{1}{2}\sum_i m_i V_i^2 = \tfrac{1}{2}\sum_i m_i (v_i + r_i \times \omega)^2$$
$$= \tfrac{1}{2}\sum_i m_i v_i^2 + \tfrac{1}{2}\omega^2 \sum_i m_i r_i^2 \sin^2 (r_i \omega)$$

is found to be free of cross terms between the two sets of variables because of (4) and:

$$\sum_i m_i v_i \cdot [r_i \times \omega] = \omega \cdot \sum_i m_i [\vartheta_i \times r].$$

[13] C. Eckart, in Phys. Rev. **46**, 383 (1934), defined the angular velocity by:

$$da_i/dt = [\omega \times a_i] \qquad (11)$$

and obtained cross terms in the kinetic energy. There, a_i is the unit vector along the i'th principal axis of inertia.

Eulerian angles θ, ψ, χ may be used to describe the motion of the rigid frame, and $(3N-6)$ internal parameters, preferably normal coordinates, may be chosen to describe the positions of the N particles relative to the frame.

Let us now consider a general system $\mathfrak{S}$ with n rotational[14] degrees of freedom, the only restriction being that the kinetic energy K of $\mathfrak{S}$ can be expressed as a quadratic form in the momenta p_i:

$$2K=\sum_{ik} a_{ik}p_ip_k. \tag{5}$$

The momentum part of the integration required by (3) can then be carried out explicitly. Considering (5) and the fact that an n-dimensional ellipsoid with the equation:

$$\sum_{ik} b_{ik}x_ix_k=1$$

has a volume v:

$$v=(\pi^{n/2}/\Gamma(n/2+1))\,|C_{ik}|^{-\frac{1}{2}}$$

it is easily seen that:

$$\int\cdots\int dp_1\cdots dp_n e^{-k/kT}=(2\pi kT)^{n/2}|a_{ik}|^{-\frac{1}{2}}.$$

Substituting this into (3) we arrive at the following formula:

$$\bar{\mu}=\int\cdots\int dq_1\cdots dq_n\mu e^{(E-f)/kT} \tag{6}$$

with

$$f\equiv v-kT\ln\left[(2\pi kT)^{n/2}|a_{ik}|^{-\frac{1}{2}}\right] \tag{6a}$$

and

$$F\equiv -kT\ln\int\cdots\int dq_1\cdots dq_n e^{-f/kT}=\bar{H}-TS. \tag{6b}$$

F and S represent the rotational free energy and entropy of the system respectively. An expression for the entropy of a molecule with internal degrees of freedom is thus obtained as a by-product of the above calculation:

$$S=k\ln\int\cdots\int dq_1\cdots dq_n \times\ln\left\{(2\pi ekT)^{n/2}|a_{ik}|^{-\frac{1}{2}}e^{(\bar{v}-v)/kT}\right\}. \tag{7}$$

As an application, the part of the molar polarization $(P-P_0)$ which is due to the presence of rotating polar groups will be computed for a compound consisting of molecules with only one internal degree of freedom, q_0. Let the potential energy be a function $V(q_0)$ in the absence of external fields, and $[V(q_0)-F\mu_z]$ in the presence of the homogeneous electric field F directed along the z axis. μ_z is a function of q_0 and represents the z component of the instantaneous electric moment of the molecule. According to (3), the mean value of the electric moment in the direction of the field is:

$$\overline{\mu_z(F)}=\frac{\int\cdots\int dq_0\cdots dp_3\mu_z e^{-H/kT}}{\int\cdots\int dq_0\cdots dp_3 e^{-H/kT}}, \tag{8}$$

where $H=H_0-F\mu_z$ is the total energy of the system. Since in the approximation valid for the weak fields of the Debye theory:

$$e^{-H/kT}=e^{-H_0/kT}[1+(F\mu_2/kT)+\cdots]$$

we have:

$$\overline{\mu_z(F)}=\overline{\mu_z(0)}+(F/kT)[\overline{\mu_z^2(0)}-\overline{\mu_z(0)}^2] =(F/3kT)\overline{\mu^2(0)}. \tag{9}$$

The kinetic energy of the molecule may be expressed in terms of the angular momentum M, resolved in the three directions of its—instantaneous—principal axes:

$$2K=p_0^2/I(q_0)+M_{\mathrm{I}}^2/A(q_0) +M_{\mathrm{II}}^2/B(q_0)+M_{\mathrm{III}}^2/C(q_0). \tag{10}$$

It is not difficult to show that evaluation of the mean square of the electric moment $\overline{\bar{\mu}^2}$ according to formula (6) leads to the following expression for the molar polarization:

$$P-P_0\equiv\frac{4\pi N}{3}\frac{\overline{\mu(F)}}{F} =\frac{4\pi N}{9kT}\frac{\int dq_0\mu^2(ABCI)^{\frac{1}{2}}e^{-v(q_0)/kT}}{\int dq_0(ABCI)^{\frac{1}{2}}e^{-v(q_0)/kT}}, \tag{11}$$

where N is the number of molecules per mole, $A(q_0)$, $B(q_0)$, $C(q_0)$ are the Eulerian moments of inertia and $I(q_0)$ is the generalized moment of inertia for the internal motion as defined by Eq. (10). Its functional relation to q_0 is such as to render Eq. (11) invariant under transformations from one internal parameter q_0 to another.

The weight factor which occurs in (11):

[14] "Rotational" degrees of freedom are characterized by full excitation at the temperature considered and may include torsional vibrations of low frequency. The translational degrees of freedom are not interesting in this connection and we assume that they have been separated off.

$$W(q_0)=(ABCI)^{\frac{1}{2}} \quad (12)$$

attributes weight to the individual configurations according to their moments of inertia. In a purely descriptive manner we may connect the variations of weight with pulsations of phase space as the volume element in momentum space occupied by a given range dK of kinetic energy changes with the changing configurations. This is the classical analog, in the sense of the correspondence principle, of the fact that the rotational energy levels are more widely spaced, and of lesser multiplicity in a certain definite energy range dK,[15] when the moments of inertia are smaller; an analog that could be made more convincing were it true that the system goes through a number of external revolutions before marked changes of the moments of inertia take place.

Before closing this section, the obvious limitations of the treatment will be emphasized:

(1) Integrals in phase space are used throughout as an approximation of the state sums. As ⊜ is in reality a quantized system, our results are valid only inasmuch as the separation between neighboring rotational levels $\Delta E \ll kT$.

(2) Our neglect of the vibrational degrees of freedom which the system may have, restricts the strict validity of the treatment to temperatures where practically all molecules are in their lowest vibrational state. At higher temperatures, Eqs. (6), (6a), (7) have to be modified so as to include the vibrational part of the entropy.

(3) Even with all the molecules in their lowest vibrational states the kinetic energy of vibration is not zero, and may vary from one configuration to the other. Inasmuch as the molecule vibrates in the neglected degrees of freedom at a much faster rate than it goes through the rotations and torsional vibrations, it is probably a good approximation to consider the interaction as an adiabatic transfer of zero-point energy to and from the other modes of motion; a picture which attributes to the zero-point energy a role similar to a potential opposing free rotation in q_0.[16] The fluctuations of zero-point energy may be estimated as contributing amounts of the order of a few hundred calories to the opposing potential, in the case of compounds such as butane, dichloroethane and others, where the observed broadening and doubling of Raman shifts has been attributed to the internal motion.[17] As equipartition of kinetic energy is more nearly approached with rising temperature, the effect should vanish or, in any event, be drowned by the concurring influence of the higher states of vibration.

II. Approximation of the Potential Function by Its First Two Fourier Components

In order to extend the integrations required by (11) to the second Fourier component of the periodic potential $V(q_0)$, we replace it by its expression (2). In terms of the azimuthal angle φ between the two revolving groups, taken around the C−C bond, the square of the instantaneous electric dipole moment in (11) is:

$$\mu^2=[2\mu_1\cos(\varphi/2)]^2=2\mu_1^2(1+\cos\varphi), \quad (13)$$

where μ_1 is the group moment of either of the two alike groups, resolved at right angles to the C−C bond. Thus it is seen that formula (11) leads to integrals of the following type:

$$I(m;x,y)\equiv(1/2\pi)\int_0^{2\pi}e^{(x\cos\varphi+y\cos 2\varphi)} \times\cos m\varphi d\varphi. \quad (14)$$

In terms of these integrals, we have:

$$\overline{\cos\varphi}=\frac{I(1;-v_1/kT,-v_2/kT)}{I(0;-v_1/kT,-v_2/kT)}. \quad (15)$$

Here, the single bar in $\overline{\cos\varphi}$ indicates that the weight factor $W(\varphi)$ has been omitted. It is practical to derive $\overline{\cos\varphi}$ as a correction of $\overline{\cos\varphi}$ at a later stage, when $W(\varphi)$ has been determined for a particular molecule, by a procedure described at the end of this section.

By expanding the exponential in the integrand of $I(m;x,y)$ into powers of x, y:

[15] This change of multiplicity results from the fact that, with the moments of inertia decreasing, rotational levels of lesser quantum number j (i.e., in the case of a simple rotator) and accordingly of lesser multiplicity $(2j+1)$ move into the contemplated energy range dK.

[16] This potential can be brought into a certain formal analogy with the binding potentials between atoms in a molecule where the quantized electronic energy varies with the internuclear distance. The variation of electronic energy provides the potential in which the nuclei are moving.

[17] F. Kohlrausch, Zeits. f. physik. Chemie **B18**, 61, also reference 5a. In typical cases, line doubling with about 100 wave numbers separation has been reported.

$$2\pi I(m;x,y)=\sum_{n,k}\frac{1}{n!}\binom{n}{k}x^{n-k}y^k\int_0^{2\pi}\cos^{n-k}\varphi(2\cos^2\varphi-1)^k\cos m\varphi d\varphi$$

$$=\sum_{n,nl}(-1)^{k-l}2^l x^{n-k}y^k\frac{1}{n!}\binom{n}{k}\binom{k}{l}\int_0^{2\pi}\cos^{n-k+2l}\varphi\cos m\varphi d\varphi$$

and changing from powers of the cosine to the cosine of the multiple angle[18] we have:

$$2\pi I(m;x,y)=\sum_{nklr}(-1)^{k-l}\frac{1}{2^{n-k+l}}x^{n-k}y^k\frac{1}{n!}\binom{n}{k}\binom{k}{l}\binom{n-k+2l}{r}\int_0^{2\pi}\cos(n-k+2l-2r)\varphi\cos m\varphi d\varphi.$$

This last sum of integrals contains only two nonvanishing contributions, namely the ones for which: $|n-k+2l-2r|=|m|$. That the two contributions are equal can be seen from the fact that, with n, k, l being fixed and $2r=n-k+2l\pm m$, the only expression which could depend on the sign of m would be $\binom{n-k+2l}{r}$. But this is also independent of the sign of m since, for every value of s, m:

$$\binom{s}{(s+m)/2}=\binom{s}{(s-m)/2}$$

if $(s-m)$ is even as in the present case. Thus, introducing a new summation index $i=(r-l)$ in place of l, and discarding all terms except the ones for which $(n-k+2l-2r)=\pm m$, we have:

$$2\pi I(m;x,y)=2\sum_{kir}(-1)^{k+i-r}\frac{1}{2^{m+i+r}}x^{m+2i}y^k\frac{1}{(m+2i)!k!}\binom{k}{r-i}\binom{m+2r}{r}\int_0^{2\pi}\cos^2|m|\varphi d\varphi$$

and finally:
$$I(m;x,y)=\sum_{ik}a^m{}_{2i,k}x^{m+2i}y^k \tag{16}$$

with
$$a^m{}_{2i,k}=\frac{(-1)^{i+k}}{2^{m+i}(m+2i)!k!}\sum_i^{i+k}{}_r\left(-\frac{1}{2}\right)^r\binom{k}{r-i}\binom{m+2r}{r}. \tag{17}$$

No separate treatment is needed for $m=0$; in this case, the sum contains only one nonvanishing integral, but its value is 2π instead of π.

The numerical evaluation of the integrals $I(m;x,y)$ is greatly simplified by the aid of recurrence formulas:

$$a^0{}_{2i,k}=(1/2i)a'_{2i-2,k} \qquad \text{for } m=0 \tag{18}$$

$$a^{m+1}{}_{2i,k}=2(m+2i+2)a^m{}_{2i+2,k}-a^{m-1}{}_{2i+2,k} \qquad \text{for } m=\pm1,2\cdots. \tag{19}$$

Only the formula for $m=0$ is needed here and will be proved:[19] If the identity between binomial coefficients:

$$\left(-\frac{1}{2}\right)^{r+1}\binom{2r+2}{r+1}=\left(-\frac{1}{2}\right)^{r+1}\binom{2r+1}{r}$$

is multiplied on both sides with $\dfrac{(-1)^{i+k}}{2^i(2i)!k!}\binom{k}{r-i}$ and if the index r is summed from $r=i$ to $r=i+k$, Eq. (18) follows at once from a comparison of the result with Eq. (17).

The higher coefficients $a^m{}_{2i,k}$ can be expressed in terms of the a^0's with the aid of (18), (19).

[18] It is readily verified that:

$$\cos^p x=(\tfrac{1}{2}p)\sum_{k=0}^{p}\binom{p}{k}\cos(p-2k)x.$$

Including into the summation negative values of $(p-2k)$ takes automatic care of the various two-factors appearing in the formula as usually stated, and makes unnecessary the customary distinction between even and odd p.

[19] The recurrence formula (18) for $m=0$ follows as a special case of (19) if use is made of the identity:

$$a^1{}_{2i,k}=a^{-1}{}_{2i+2,k}.$$

This, in turn, springs directly from a comparison of corresponding powers in the equation [see definition (14) of $I(m;x,y)$]:

$$I(1;x,y)=I(-1;x,y).$$

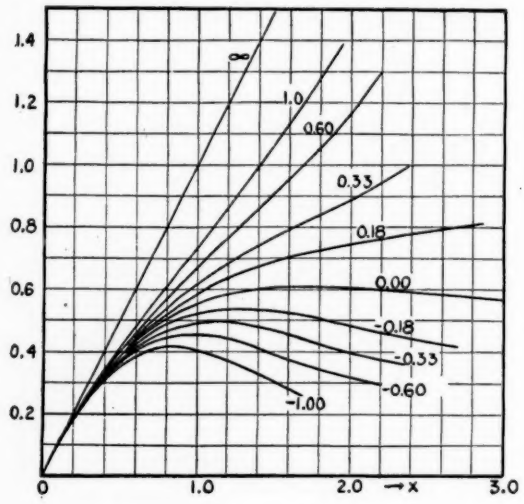

FIG. 1. $p_\rho(x)$.

Formula (18) reduces the numerical labor necessary for evaluation of $I(l; x, y)$ and $I(0; x, y)$ to exactly the half amount.

We are now ready to calculate the polarization (11), omitting the weight factor W for the time being. Substituting (13) into (11) we have:

$$P-P_0=(8\pi N/9kT)\mu_1^2(1+\overline{\cos\varphi}). \quad (20)$$

This shall be written:

$$p_\rho(x)=x[1+I(1; x, \rho x)/I(0; x, \rho x)], \quad (21)$$

where

$$p_\rho(x)\equiv(9v_1/8\pi N\mu_1^2)(P-P_0),$$

$$\rho\equiv v_2/v_1, \quad x\equiv -v_1/kT$$

and

$$I(m; x, \rho x)=\sum_{ik}(a^m{}_{2i,\,k}\rho^k)x^{m+2i+k}. \quad (22)$$

The curves $p_\rho(x)$ have been calculated from (21), (16), (17) and are plotted in Fig. 1. The experimental values $(P-P_0)$ may now be plotted against T^{-1} in such a manner that, upon suitable choice of scale factors $a=9v_1/8\pi N\mu_1^2$, $b=v_1/k$ the closest possible fit is attained between the points $a(P-P_0)$ plotted *vs.* bT^{-1} on one hand, and one of the curves $p_\rho(x)$ on the other. This matching fixes the numerical value of ρ and thus determines the shape of the potential (2). Its absolute magnitude, expressed by V_1, as well as the group moment μ_1, are determined simultaneously from the two scale factors a, b used in the process of matching. The curve $p_0(x)$, labeled 0.00 in Fig. 1, is the same as has been previously obtained by different workers. It permits expression in terms of Bessel functions:

$$p_0(x)=x(1+iJ_1(ix)/J_0(ix)).$$

Because of the poor convergence of (22) for large x (low temperatures), the numerical evaluation of the curves $p_\rho(x)$ is quite laborious; up to 16 powers had to be used. Thus, a discussion of the asymptotic behavior of the curves for large x supplements the calculations in a helpful way. The position of the absolute minimum of the potential (2) decides the limiting value which the resulting dipole moment of the molecule approaches for low temperatures, and determines the limiting slope of the p curves for large x. Since, for $\rho<0$, both terms of V have their minimum value at $\varphi=180°$, the most stable position is always the trans position; hence no dipole moment and zero slope of the curves as x goes to infinity. In the case of positive ρ, however, a shift of the absolute minimum may take place. A distinction is found necessary between the two cases $\rho\lessgtr 0.25$.

(a) $\rho<0.25$: At very low temperatures, practically all molecules are found in the immediate neighborhood of the trans position $\varphi=180°$. A Taylor expansion around $\varphi=180°$ shows that the potential there behaves qualitatively as in the case $\rho=0.0$:

$$v(\pi-\epsilon)=-v_1(1-\rho)+v_1(1-4\rho)\epsilon^2/2+\cdots.$$

Correspondingly, it is found by a short calculation that the curves $p_\rho(x)$ go asymptotically to a constant value $1/2(1-4\rho)$.

(b) $\rho>0.25$: In this case the minimum is shifted from $\varphi=180°$ to two positions $\varphi=\arccos(-1/4\rho)$, symmetrically spaced around the trans position. Hence, the dipole moment approaches a lower limit

$$\overline{\mu(F)}/F=\overline{\mu^2}/3kT\to(2\mu_1^2/3kT)(1-1/4\rho)$$

and the limiting slope of the p-curves is found to be:

$$\lim_{x\to\infty}(d/dx)p_\rho(x)=(1-1/4\rho).$$

The Fig. 1 shows the different behavior of the curves in both cases quite markedly. It is hardly necessary to emphasize that our classical treatment does not really apply to the limiting case of low temperature, and gives consistently lower polarizations than would a quantum-mechanical treatment. In the experimentally accessible range of temperature, however, such deviations are, in all probability, very small.

A few words are necessary concerning the computation of $\overline{\cos\varphi}$. When the weight factor $W(\varphi)$ has been determined for a particular molecule, and provided its deviations from unity: $\Delta W=(W-1)$ are found small so that the influence of W on (11) has the character of a correction applicable to $\overline{\cos\varphi}$, it is expedient to carry out the integration (11) in the two steps indicated by the following:

$$\overline{\cos\varphi}=(I_1+\Delta I_1)/(I_0+\Delta I_0), \qquad (23)$$

where

$$I_0+\Delta I_0\equiv\frac{1}{2\pi}\int_0^{2\pi}d\varphi W(\varphi)e^{x\cos\varphi+y\cos 2\varphi}$$

$$=I(0;x,\rho x)+\frac{1}{2\pi}\int_0^{2\pi}d\varphi\Delta We^{x(\cos\varphi+\rho\cos 2\varphi)},$$

$$I_1+\Delta I_1\equiv\frac{1}{2\pi}\int_0^{2\pi}d\varphi W(\varphi)\cos\varphi e^{x\cos\varphi+y\cos 2\varphi}$$

$$=I(1;x,\rho x)+\frac{1}{2\pi}\int_0^{2\pi}d\varphi\cos\varphi\Delta W\cdot e^{x(\cos\varphi+\rho\cos 2\varphi)}.$$

By a suitable choice of the integration parameter q_0, the corrections ΔI_0 and ΔI_1 can be kept small compared with the main terms $I(0;x,y)$ and $I(l;x,y)$, and can be found by graphical integration with sufficient accuracy to match the accuracy of the series expansion attainable for the main terms. The overall accuracy obtained with the combined use of explicit formulas and graphical integration was sufficient to compare with the accuracy of the best experimental results.

TABLE I.

	φ	A^*	B	C	$(ABC)^{\frac{1}{3}}$	I^*	W	ΔW
cis:	0°	154.8	219	70.7	1560	9.70	0.6827	−0.3173
	15						.730	− .270
	30	167.2	226.1	68.1	1600	13.9	.8363	− .1637
	45						.960	− .040
	60	204.9	248.6	59.5	1745	19.16	1.070	.070
	75						1.150	.150
	90	267.0	287	42.4	1800	22.64	1.200	.200
	105						1.190	.190
	120	320.5	327.3	31.7	1830	19.36	1.132	.132
	135						1.023	.023
	150	353.6	347.2	20.7	1600	18.24	.9557	− .044
	165						.950	− .050
trans:	180	377		365.5	17.6	1560	19.70	.9650 − .035

* The moments of inertia in this table are expressed in the units: Hydrogen mass at one Angstrom distance. C is the moment around the principal axis closest to the C−C bond.

TABLE II.

φ	$\bar{\varphi}$	$d\varphi/d\bar{\varphi}$	$\overline{W}(\bar{\varphi})$
0	0	1.8	1.21
30	18	1.78	1.47
60	36	1.7	1.79
90	55	1.4	1.65
120	80	1.0	1.11
150	116.5	.7	.66
180	180	.3	.28

III. Application to 1,2-Dichloroethane

The results of the preceding two sections have been applied to dichloroethane with the help of graphical methods. The determination of the moments of inertia $A(q_0)$, $B(q_0)$, $C(q_0)$ is greatly facilitated if we note that the molecule has, for every one configuration, what may be termed an inversion axis X; i.e., an axis which permits rotation of the whole molecule by 180° as a covering operation. This property makes the axis X automatically a principal axis of inertia, since projections of the system into any plane containing X are symmetric with respect to X. On the strength of this fact, the process of locating the principal axes for a particular configuration of the molecule reduces to finding the two remaining ones, i.e., a problem in two dimensions.

The customary distances, namely 1.52A, 1.85A and 1.08A, were used for the distances between C−C, C−Cl and H−C, respectively. It was assumed that the two CH_2Cl groups revolve around the C−C bond with constant valence angles. Actually, considerable distortion of the tetrahedral angle C−C−Cl would be necessary to let the two Cl atoms pass by each other in the *cis* configuration. I requires an increase of 7° to raise the distance of closest approach from

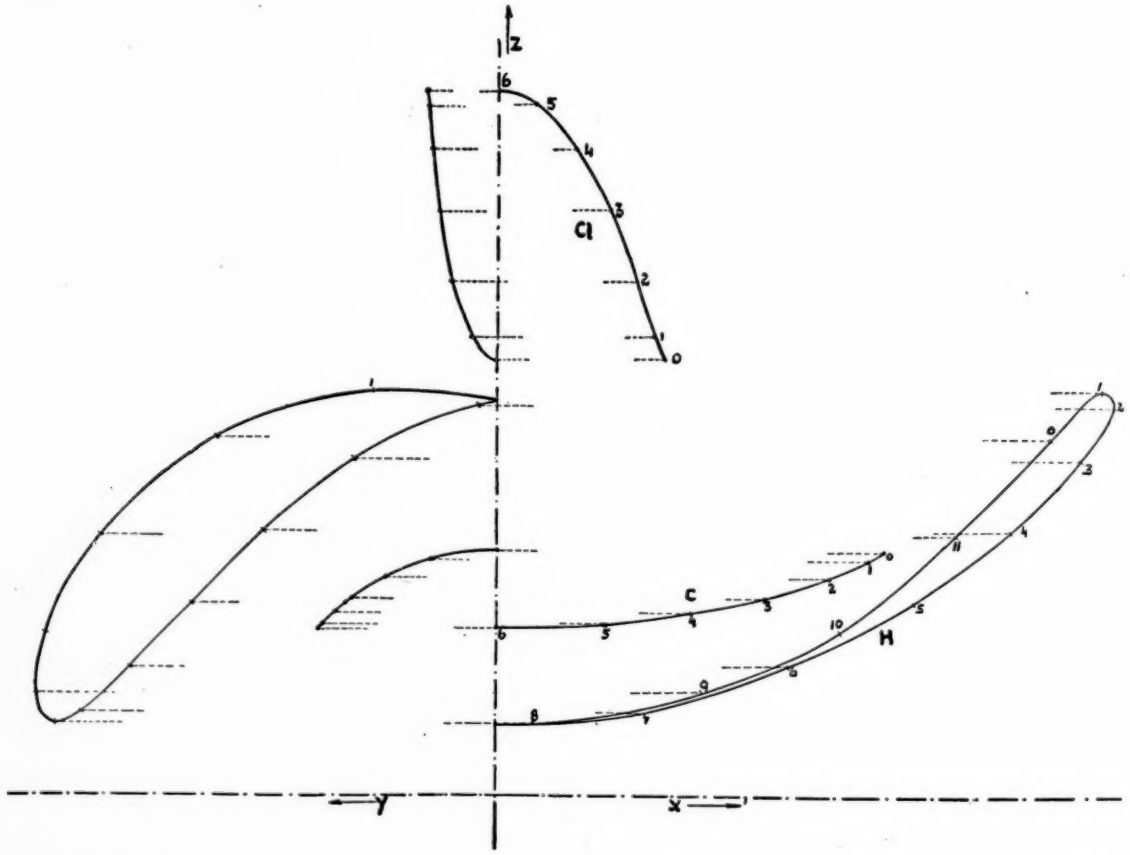

FIG. 2. Orbits of the constituent atoms of dichloroethane described in "internal" motion. The H orbit is the same for both hydrogen atoms in the same group, positions occupied simultaneously are: 0–0, 1–11, 2–10, etc.

2.7A to the observed 3.2A; a distortion which has been ignored here, both in the calculation of A, B, C as in the effect which it must have on the validity of Eq. (13). This neglect tends to raise the calculated polarization at high temperatures where distortion plays a part, as is born out, later on, by a comparison with the experimental values.

Next, the moment of inertia $I(\varphi)$ had to be determined. From its definition (10) it follows that:

$$K_{\text{int}} = p_\varphi^2/2I = (\dot{\varphi}^2/2)\sum_i m_i(dx_i/d\varphi)^2,$$
$$I(\varphi) = \sum_i m_i(dx_i/d\varphi)^2. \tag{24}$$

The derivatives $dx_i/d\varphi$ were determined graphically in the following manner: The orbits were constructed which the individual atoms of the molecule describe, relative to a reference frame $X_i=(X, Y, Z)$ defined by the Eq. (4). This relative motion is the one which was referred to as "internal" motion in the earlier part of section I. The orientation of the frame relative to the molecule is completely described by two geometrical requirements: For any instantaneous configuration, the X axis can be identified with the inversion axis, and the Z axis taken as the straight line through the two centers of gravity of the two CH_2Cl groups. During the motion, the centers of gravity slide back and forth along the Z axis while equal and opposite revolutions around it are executed by the two groups.

During each complete revolution in space the molecule goes through two *cis* positions in the XZ plane, and through two *trans* positions in the YZ plane; two successive *cis* positions marking a full period 2π of the parameter φ. Thus it is seen that all orbits are symmetrically arranged with respect to any of the three coordinate planes. It is then sufficient for a full

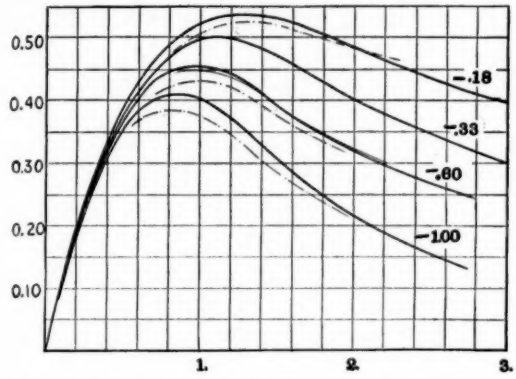

FIG. 3. Curves $p_\rho(x)$ with corrections $\Delta W'$ applied, (broken curves). The weak curve near $\rho=-0.60$ is corrected with ΔW.

description of the motion in space to present two views of one octant, using the conventional methods of descriptive geometry. The dots 0, 1, $2\cdots$ in Fig. 2 represent those configurations for which φ equals a multiple of 30°. A third view, looking down along the Z axis can be readily obtained and provides us with the functional relation between our parameter φ and the one used by Lennard-Jones and Pike in their treatment of the same problem. This latter parameter $\bar{\varphi}$ measures the azimuthal angle between the two C−Cl bonds around the Z axis; a list of corresponding values of φ and $\bar{\varphi}$ is given in Table II for later reference.

From Fig. 2 the coordinates x_i of the eight atoms in their positions 0, 1, $2\cdots$ have been measured and the derivatives $dx_i/d\varphi$ determined by numerical differentiation.[20] In terms of these, I was determined from (24) and is listed in Table I. W was next calculated and normalized so that:

$$\int_0^{2\pi} d\varphi W(\varphi)=1,$$

The values of $W(\varphi)$ for odd multiples of 15° in Table I were then found by interpolating between the calculated ones. With the values ΔW determined, the weight factor could now be applied to the $p_\rho(x)$ curves, using (23).

The correction, when applied to $p_{-0.60}(x)$, results in the weak curve accompanying the fully drawn curve in Fig. 3. The correction is surprisingly small, so that it was considered

[20] Runge and Koenig, *Vorlesungen ueber numerisches Rechnen*, p. 76.

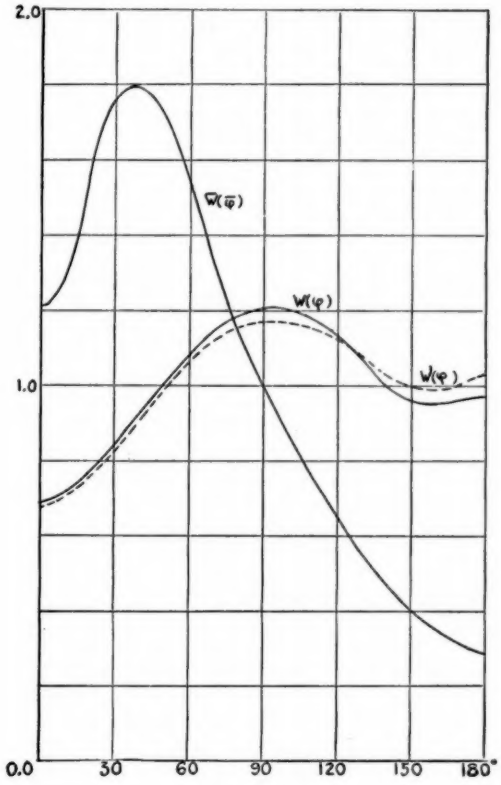

FIG. 4.

unnecessary to apply the same lengthy process to the other curves. That the weighing with W is, in general, an affair by no means trivial but results in noticeable corrections of the p curves, is demonstrated by setting up an artificial weight factor $W'(\varphi)$, Fig. 4, which, for demonstration's sake, has been given slight deviations from $W(\varphi)$. The corrections obtained for $p_\rho(x)$ with $W'(\varphi)$ are given for a few ρ values as the broken curves in Fig. 3, showing that small changes are not the rule but constitute a specific advantage of our choice of parameter.

Lennard-Jones and Pike,[4] have taken a different choice, arguing that the motion in space is not around the C−C bond and that the azimuthal angle should more properly be taken around the axis of revolution. A comparison of results of the two treatments is therefore in order. Clearly, this method is sufficiently general to permit the choice of either φ or $\bar{\varphi}$, since integration over the conjugate momentum makes the results invariant under transformations from one to the other. With this proviso, the question

TABLE III.

ρ	$\mu_1 DU$	$2V_1$
0.0	1.75	$2.06.10^{-13}$ erg
− .18	1.57	1.48
− .33	1.53	1.26
− .60	1.48	1.14
−1.00	1.46	0.96

reduces to one of mere convenience. However, attention must be given to the significance of the potential function V when comparing results, since obviously $V_1 \cos \bar{\varphi}$ means something quite different from $V_1 \cos \varphi$. If the values φ are substituted from Table II, the potential function $V_1 \cos \bar{\varphi}$ adopted by Lennard-Jones and Pike is a function of φ as pictured in Fig. 5, curve B. In the calculation of the polarization with a potential $V_1 \cos \bar{\varphi}$, a weight factor $\overline{W}(\bar{\varphi})$ should be used which follows from the formula:

$$\overline{W}(\bar{\varphi}) = W(\varphi) d\varphi / d\bar{\varphi}.$$

φ and $\bar{\varphi}$ in this formula are corresponding parameter values referring to the same configuration. Numerical evaluation has given the values $\overline{W}(\bar{\varphi})$ listed in Table II and plotted in Fig. 4. It would seem that omission of this weight factor must modify the conclusions reached.

These advantages were found in choosing φ as our parameter: It permits a direct and physically significant expression of the potential; an expression which, in particular, does not depend upon the mass distribution in the molecule. The dipole moment μ bears a simple relation to φ and thus complications are avoided. The main advantage in working with φ is that it permits use of the p curves as polarization curves without laborious corrections.

Next it must be found which curve $p_\rho(x)$ gives the best agreement with Zahn's experimental values $(P-P_0)$ for dichloroethane.[1] To be acceptable, this choice must also lead to reasonable conclusions regarding μ_1 and $2V_1$. (It has been shown, above, how these two quantities are determined in the matching process.) Table III gives a list of values required to establish coincidence between the maxima of the experimental curve and the corresponding $p_\rho(x)$ curve.

Of the potentials (2) admitted for comparison, the following (Fig. 5, curve A) has been found to give closest agreement with Zahn's measurements:

$$V = (0.57 \cos \varphi - 0.34 \cos 2\varphi) \cdot 10^{-13} \text{ erg}. \quad (25)$$

It involves a ratio $\rho = -0.60$ and a group moment $\mu_1 = 1.48 \cdot 10^{-18}$ e.s.u. The temperature dependence of $(P-P_0)$ calculated with (25) is shown in Fig. 6, together with the experimental points.

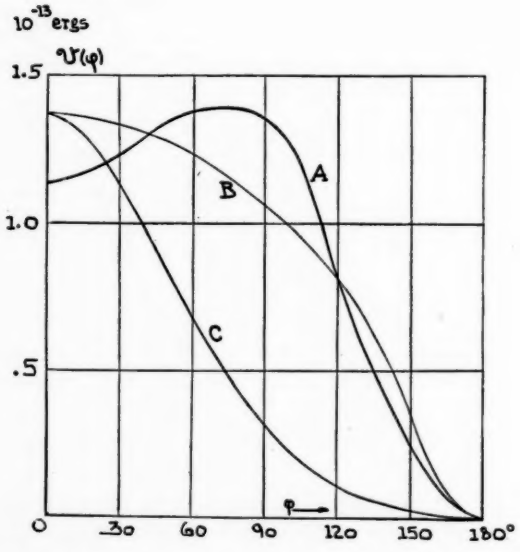

FIG. 5. Curve A: $V(\varphi) = 0.571 \cos \varphi - 0.34 \cos 2\varphi$; Curve B: Lennard-Jones and Pike's potential; Curve C: Electrostatic potential according to Smyth, Dornte and Wilson.

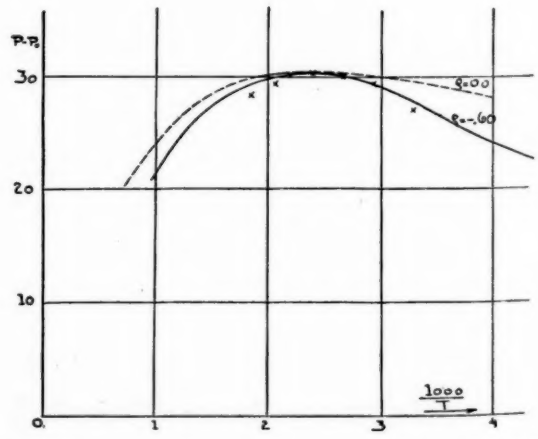

FIG. 6. Comparison between the measured values $(P-P_0)x$ and the calculated curves $p_0(x)$ and $p_{-0.60}(x)$.

Discussion of results

The improvement obtained with the incorporation of a second Fourier component is seen from a comparison with the broken curve in Fig. 6. This curve shows the best agreement that can be obtained on the basis of $p_0(x)$. Marked deviations result from the relative flatness of $p_0(x)$; deviations which are greatly reduced though not completely avoided when $p_{-0.60}$ is used instead. The deviations of $p_{-0.60}$ at high temperatures (small x) can in part be attributed to the neglect of valence angle distortion. In principle, however, they indicate to the author's mind a steeper potential rise, upon approaching the *cis* position, than is exhibited by (25). The potential V could rise more steeply from 90°, say, toward 0° without appreciable change of the statistical distribution at lower temperatures, where few groups penetrate into the near *cis* region anyway. At temperatures around 500°K, however, the configurations near the *cis* position gain in statistical weight. Failure of (25) to represent the potential rise in its full steepness must then raise the calculated values of the mean dipole moment. According to Fig. 6, this appears to be the case. Thus it is not likely that the potential minimum in the *cis* position is significant though it seemed to offer an interesting and tempting possibility, in view of other experimental data which had been interpreted in the past as proving the existence of two stable forms of dichloroethane.[21]

The rise of the potential from the *trans* position, ($\varphi=180°$) is surprisingly steep. Up to about 150°, it must certainly be attributed to repulsion between either of the two Cl atoms and the closer H atom belonging to the other group. Upon further approach of the *cis* position, however, a very appreciable portion of the total repulsion must be due to Cl−Cl repulsion. This seems to establish the existence of repulsive forces between two bound Cl atoms at larger distances than is usually assumed; in fact, there must be considerable repulsion at a distance of 4.0A($\varphi=120°$). No further attempt is made here to interpret the potential (25) in detail. Calculations, based on such theoretical assumptions as can be made at present with regard to Cl−Cl, Cl−H and H−H interaction, yield a total potential V in fair agreement with (25). It is expected to present these calculations in a separate note.

IV. *Cis* and *Trans* Dichloroethylene

The results of section III are likely to throw new light on a problem which has arisen from other experimental sources, namely the question of the relative stability of the two isomers of dichloroethylene. The thermal equilibrium ratio of the two forms has been determined by Ebert and Büll[22] as 63 percent *cis* to 37 percent *trans* at 300°C, and has been interpreted as demonstrating that the potential energy of the *trans* form exceeds that of the *cis* form by approximately 600 cal/mole; a situation both unusual and unexpected in view of the strong intramolecular repulsion which manifests itself in the similar case of dichloroethane. Hence the present writer has felt reluctant to accept this interpretation, in spite of theoretical arguments brought forward by H. A. Stuart and intended to make plausible the greater energy of the *trans* form.[23] Stuart's omission of repulsive potentials other than electrostatic is a disputable point, considering that an appreciable part of the repulsive energy in dichloroethane had to be attributed to Cl−Cl steric repulsion. To get some indication about the energy difference between the two forms by comparison with dichloroethane, we note that the Cl−Cl distance in the latter is very nearly the same at $\varphi=90°$ as in *cis*-dichloroethylene, and only slightly shorter at $\varphi=180°$ than it is in *trans*-dichloroethylene. Obviously, only part of the repulsive forces active in dichloroethane

[21] Wierl's contention that two stable forms exist was based on his electron diffraction data which seemed to suggest two definite spacings of Cl−Cl at 3.2 and 4.4A. Ehrhardt's investigation of dichloroethane with x-rays, however, suggested a continuous distribution of spacings as a more likely alternative (Physik. Zeits. **33**, 605 (1932)). Also, the doubling of Raman shifts in molecules $X-CH_2-CH_2-X$, observed by Kohlrausch (Zeits. f. physik. Chemie **B18**, 61, originally attributed to the presence of essentially two configurations, can be reconciled with the idea of a continuous distribution, following an argument by Mizushima, Morino and Higasi, Physik. Zeits. **35**, 905 (1934).

[22] Ebert and Büll, Zeits. f. physik. Chemie **A152**, 451 (1931).

[23] H. A. Stuart, Physik. Zeits. **32**, 793 (1931); also the same author's book *Molekülstruktur*, Springer, Berlin. Stuart's calculation would give an even larger difference: $v_{trans}-v_{cis}=1150$ cal.

TABLE IV.

Cl–Cl distance in A	Energy of interaction $\times 10^{14}$/ergs: Dipole effect	Induction effect	Steric repulsion minus Van der Waals attraction:	Total
cis: 3.6	+8.4	−7.7	+4.0 (−4.8)*	+4.7 (−4.1)
trans: 4.6	+4.9	0	0 (−1.1)	+4.9 (+3.8)
			Difference	− 0.2 (−7.9)

* The *trans* position is arbitrarily assumed as having zero "steric" potential.

will be found present in dichloroethylene, on account of the absence of two H atoms. Let us roughly assume that 30 percent of the repulsive energy of the former, taken at $\varphi=90°$, is a conservative estimate for the increase in "steric" potential of dichloroethylene when going from the *trans* to the *cis* form. This would suggest the following changes in Table IV originally given by Stuart,[22] with his original figures retained in brackets for comparison where changes have been made. Thus we find the energies of the two forms equal within the accuracy of the estimates made. A possible difference in the vibrational zero-point energies may affect this result one way or the other by small amounts. Far from agreeing with the result reported by Ebert and Büll, this merely serves to accentuate the difficulty which Stuart wished to explain. The following has now occurred as a likely explanation: By reasoning in very much the same manner as in part I, one is led to the following formula for the equilibrium ratio r between the two forms:

$$r=\frac{c_{cis}}{c_{trans}}=\frac{(ABC)^{\frac{1}{2}}\,cis}{(ABC)^{\frac{1}{2}}\,trans}e^{-\Delta v/kT}. \qquad (26)$$

The principal moments of inertia have been determined, assuming a valence angle of 130° for C=C−Cl, and it was found that:

$$(ABC)^{\frac{1}{2}}{}_{cis} : (ABC)^{\frac{1}{2}}{}_{trans}=1.65$$

$$=62.3 \text{ percent} : 37.7 \text{ percent}.$$

This means that an isomeric equilibrium ratio which is very nearly equal to the one observed must be expected even in the complete absence of any heat of reaction ΔV. Generally, for temperatures high enough so that: $\Delta V \ll kT$, this ratio should represent a limiting value. It must not be forgotten, however, that here as in our previous discussions, the excitation of vibrational states is apt to modify the ratio. Among such effects are a possible change of the moments of inertia with T and the change of distribution of kinetic energy among the vibrational states at various temperatures.

The author wishes to express his thanks to Professor J. E. Lennard-Jones, for the hospitality kindly extended to him at the Chemistry College, University of Cambridge, where this study was begun; also to those members of the Universities of Cambridge, Harvard, Massachusetts Institute of Technology and Princeton with whom he has had the opportunity of discussing various phases of it.

Molecular Constants and Potential Energy Curves for Diatomic Molecules[1]

MAURICE L. HUGGINS, *Department of Chemistry, The Johns Hopkins University*

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By using the function $U=Ce^{-a(r-r_e)}-C'e^{-a'(r-r_e)}$ with $C=10^{-12}e^{-a(r_e-r_{12})}$, and taking $a=6.0\times10^8$ cm^{-1}, r_{12} values calculated from the band spectrum constants are nearly the same (1.46A) for all except highly excited states of all diatomic molecules containing only elements in the first row of the periodic table and having 12 or more electrons. This indicates that the repulsive term is nearly the same in all of these cases. This relation enables one to calculate, from experimental values of two of the molecular constants (e.g., ω_e and $\omega_e x_e$) the magnitudes of others (e.g., r_e, B_e and α). Calculated values of $\omega_e y_e$ and $\omega_e z_e$ are invariably small but not zero. The dissociation energy is (empirically) about 0.8 $(C'-C)$, calculated using $a=4.0\times10^8$ cm^{-1}.

INTRODUCTION

MORSE'S equation[2] for the potential energy of a diatomic molecule as a function of the internuclear distance has been found very useful by band spectroscopists and others. This equation may be written in the form

$$U=Ce^{-a(r-r_e)}-C'e^{-a'(r-r_e)} \qquad (1)$$

with $a=2a'$ and $C'=2C$. (Since at $r=r_e$

$$dU/dr=a'C'-aC=0 \qquad (2)$$

these two relationships between the constants are not independent.)

By relating the constants in this way Morse was enabled to solve the wave equation, obtaining from the solution an equation for the energy levels,

$$E_v/hc=E_e/hc+\omega_e(v+\tfrac{1}{2})-\omega_e x_e(v+\tfrac{1}{2})^2 \qquad (3)$$

agreeing approximately with that usually deduced from the spectra. Although additional terms, $\omega_e y_e(v+\frac{1}{2})^3$ and $\omega_e z_e(v+\frac{1}{2})^4$, are sometimes needed to represent the experimental data accurately, $\omega_e y_e$ and $\omega_e z_e$ are nearly always negligibly small in comparison with ω_e and $\omega_e x_e$.

The values of the constants in Morse's equation can be calculated from ω_e and $\omega_e x_e$ in which case the calculated dissociation energy, $C'-C$, is usually quite far from the true value as obtained in other ways. On the other hand the constants of the equation can be obtained from ω_e and the dissociation energy, the calculated value of $\omega_e x_e$ then being inaccurate. Apparently a single equation of the Morse type is not accurately correct over the whole range of distance from r_e to ∞. This is not surprising in view of the simplicity of the function and the somewhat arbitrary relation between the constants.

For different electronic states of the same diatomic molecule not only does the attractive potential vary widely but so also does the repulsive potential. It would seem more reasonable that the repulsion should vary but little from state to state. It may be noted that for the alkali halide crystals a repulsion term of the form $Ce^{-a(r-r_{12})}$ has been found[3] to be satisfactory for calculations of lattice energies and interatomic distances, with the same value of a for all these crystals. The constants r_{12} are different for different crystals but are additive.

Considerations such as the foregoing led the writer to derive and test a modification of Morse's equation, in which the repulsive term is the same for all electronic states of a particular molecule. In so doing, several interesting and useful relationships between the molecular constants have been deduced and compared with the experimental data.

SUMMARY OF METHODS AND RESULTS

Putting $$C=ce^{-a(r_e-r_{12})} \qquad (4)$$

we have $$Ce^{-a(r-r_e)}=ce^{-a(r-r_{12})}. \qquad (5)$$

[1] Preliminary reports of this work have been made at the Washington (1933), Cleveland (1934) and New York (1935) meetings of the American Chemical Society.

[2] P. M. Morse, Phys. Rev. **34**, 57 (1929).

[3] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932); J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932); M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

TABLE I.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
FORMULA	STATE	ω_e EXP.	$\omega_e x_e$ EXP.	$\omega_e x_e$ CALC. FROM r_e ($a=6$)	$\omega_e x_e$ CALC. FROM D_e ($a=4$)	a' FROM $\omega_e x_e$ ($a=6$)	D_e EXP.	$(C'-C)$ FROM $\omega_e x_e$ ($a=6$)	$0.8\,(C'-C)$ FROM $\omega_e x_e$ ($a=4$)	D_e FROM MORSE'S EQUATION	C' FROM $\omega_e x_e$ ($a=6$)	C FROM $\omega_e x_e$ ($a=6$)	r_{12} FROM $\omega_e x_e$ ($a=7$)	r_{12} FROM $\omega_e x_e$ ($a=6$)	r_{12} FROM $\omega_e x_e$ ($a=4$)	r_e EXP.	r_e FROM $r_{12}=1.46$ ($a=6$)	α EXP.	α FROM $\omega_e x_e$ ($a=6$)	α FROM MORSE'S EQUATION	REF.[1]
		(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	($10^8\,cm^{-1}$)	(e.v.)	(e.v.)	(e.v.)	(e.v.)	(10^{-12} erg)	(10^{-12} erg)	(10^{-8} cm)	(10^{-8} cm)	(10^{-8} cm)	(10^{-8} cm)	(10^{-8} cm)	(cm^{-1})	(cm^{-1})	(cm^{-1})	
C_2	$d\ ^1\Pi_g$	1832.45	34.01	10.7		4.33		2.9	2.3	3.0	16.3	11.75	1.47	1.66	imag	1.251	1.05	0.0255	0.034	0.035	
	$B\ ^3\Pi_g$	1792.55	19.35	10.0	(23)	2.02	(3.1)	5.9	3.8	5.1	14.1	4.74	1.41	1.52	2.45	1.261	1.20	.0173	.024	.024	
	$b\ ^1\Pi_u$	1608.31	12.10	6.9	(17)	.72	(3.4)	13.2	5.2	6.6	23.9	2.87	1.41	1.49	1.95	1.315	1.28	.0174	.019	.017	
	$A\ ^3\Pi_u$	1641.55	11.67	6.8	(12)	.64	(5.5)	15.5	5.7	7.1	27.6	2.94	1.40	1.49	1.94	1.308	1.28	.0149	.019	.016	
N_2^+	$B\ ^2\Sigma_u^+$	2419.84	23.190	17.1	49.0	3.30	3.1	7.6	5.8	7.8	26.8	14.75	1.36	1.52	imag	1.071	1.01	.025	.025	.025	2
		2173.2	10.43			.75		27.0	10.9		49.1	6.14					1.16		(.014)	(.013)	3
	$X\ ^2\Sigma_g^+$	2207.19	16.136	15.7	17.7	1.94	6.2	10.8	6.9	9.3	25.4	8.22	1.34	1.45	2.36	1.113	1.11	.02	.020	.019	2, 3
N_2	$C\ ^3\Pi$	2044.70	26.047	15.6		3.79		4.8	3.7	5.0	20.5	12.95	(1.40)	(1.57)	imag	(1.14)	1.03	(.032)	(.027)	(.027)	
	$B\ ^3\Pi_{reg}$	1732.84	14.437	14.7		1.60		8.1	4.8	6.4	17.5	4.67	1.35	1.46	2.13	1.201	1.20	.023	.020	.019	
	$a\ ^1\Pi_u$	1692.28	13.318	14.7	11.7	1.36	5.7	9.0	5.0	6.6	18.6	4.21	1.35	1.45	2.05	1.209	1.22	.021	.019	.018	3
	$A\ ^3\Sigma$	1460.39	13.929	10.3		1.48		6.2	3.5	4.7	13.1	3.24	1.39	1.48	2.10	1.289	1.26	.013	.019	.018	4
	$X\ ^1\Sigma_g^+$	2359.60	14.445	15.5	17.1	1.60	7.34	14.9	8.8	11.9	32.4	8.65	1.33	1.45	2.18	1.092	1.10	.018	.018	.017	3
O_2^+	$b\ ^4\Sigma_g^-$?	1198.1	17.8		(13)	2.78	(2.5)	2.5	1.8	2.5	7.5	3.47					1.25				
	$A\ ^2\Pi_u$	898.9	13.7	11.4	13.1	1.85	1.4	2.1	1.3	1.8	4.9	1.52	1.40	1.48	2.18	1.41	1.39	.014	.020	.019	
	$a\ ^4\Pi_u$?	1037.2	11.1		(10)	1.23	(2.6)	4.3	2.2	3.0	8.6	1.76					1.37				
	$X\ ^2\Pi_{greg}$	1876.4	16.53	14.2	12.9	2.49	6.15	6.9	4.8	6.6	18.8	7.80	1.35	1.48	imag	1.14	1.12	.009	.019	.018	
O_2	b	1121	17			2.60		2.4		2.3	6.7	2.88					1.28				
	$B\ ^3\Sigma_u^-$	710.14	11.705	5.0	12.1	1.38	0.95	1.8	1.0	1.3	3.7	.85	1.51	1.57	2.04	1.599	1.49	.014	.017	.016	
	E	1454	12			1.45		7.1		5.4	15.0	3.62					1.25				
	D	1524	12			1.45		7.8		6.0	16.5	3.98					1.23				
	C	1494	12			1.45		7.5		5.7	15.8	3.83					1.24				
	$A\ ^1\Sigma_u^-$?	1432.615	13.925	25.7	13.4	1.90	3.47	5.3	3.4	4.5	12.4	3.92	1.35	1.45	2.26	1.223	1 23	.0188	.018	.018	
	$X\ ^3\Sigma_g^-$	1584.91	11.645	23.9	11.4	1.35	5.09	9.1	5.0	6.7	18.7	4.22	1.34	1.44	2.05	1.204	1.22	.016	.015	.015	
F_2	$^1\Sigma$	977	141	2		21.6		.3	0.3	.2	− .2	− .6	imag	imag	imag	1.45			.050	.049	5
	$^1\Pi$	1139.8	9.7	11.7		1.34		5.6	3.1	4.1	11.6	2.6	1.35	1.44	1.99	1.28	1.30	.014	.013	.012	5
CN	$B\ ^2\Sigma^+$	2164.15	20.25	14.9	16.9	2.45	6.30	7.6	5.3	7.2	20.4	8.33	1.37	1.50	imag	1.148	1.11	.02215	.024	.024	
	$A\ ^2\Pi_{inv}$	1788.66	12.883	11.4	12.8	1.05	5.74	12.1	5.8	7.7	19.8	4.07	1.37	1.47	2.01	1.236	1.23	.01746	.018	.017	
	$X\ ^2\Sigma^+$	2068.79	13.176	14.0	14.1	1.11	7.09	15.3	7.6	10.0	25.0	5.51	1.35	1.45	2.03	1.169	1.18	.0173	.018	.017	
BeO	$E\ ^?\Sigma$	1006	10	>12		.24		14.8	2.7	3.1	24.6	.98	>1.41	>1.47	>1.79	>1.47	1.46		<.022	<.020	7
	$D\ ^?\Sigma$	1136	10			.24		19.0	3.4	4.0	31.4	1.26					1.42				
	$C\ ^1\Sigma^+$	1370.81	7.76	10.2	7.8	−.19	7.5	−35.	7.5	7.5	−53.8	1.70	1.38	1.45	1.78	1.358	1.37	.016	.018	.013	7
	$B\ ^1\Pi$	1127.77	8.401	1.8	8.1	−.07	4.7	−64.	4.4	4.7	−100.6	1.17	1.50	1.49	1.81	1.468	1.43	.01607	.019	.015	7
	$A\ ^1\Sigma^+$	1486.87	11.70	10.8	10.0	.57	5.8	13.7	4.6	5.8	24.0	2.28	1.39	1.47	1.89	1.327	1.32	.0189	.021	.018	7
BO	$B\ ^2\Sigma^+$	1280.3	10.07	17.4	(12)	.51	(3.26)	12.9	4.1	5.0	22.4	1.91	1.33	1.41	1.81	1.301	1.35	(.017)	.020	.017	
	$A\ ^2\Pi_{inv}$	1297.13	11.61	13.2	(11)	.70	(3.7)	9.0	3.5	4.5	16.3	1.90	1.37	1.45	1.87	1.343	1.35	.0211	.021	.019	8
		1260.42	10.94	12.7	(11)	.70	(3.7)	9.1	3.5	4.5	16.4	1.90	1.37	1.45	1.87	1.342	1.35	.0196	.019	.017	8
	$X\ ^2\Sigma^+$	1940.26	12.48	14.1	(13)	.87	(6.6)	16.3	7.2	9.3	30.3	4.39	1.35	1.45	1.96	1.203	1.21	.0177	.019	.017	8
		1885.44	11.77	13.4	(13)	.86	(6.6)	16.5	7.2	9.3	30.6	4.39	1.35	1.45	1.96	1.202	1.21	.0165	.018	.016	8
CO^+	$B\ ^2\Sigma^+$	1722.1	24.33	20.6	25.4	3.31	2.68	3.8	2.9	3.8	13.4	7.38	1.35	1.49	imag	1.16	1.13		.030	.030	
	$A\ ^2\Pi_{inv}$	1564.53	14.07	14.9	12.4	1.39	4.58	7.4	4.1	5.4	15.3	3.56	1.36	1.45	2.05	1.24	1.25		.020	.019	
	$X\ ^2\Sigma^+$	2212	15.17	16.7	15.6	1.61	7.1	12.8	7.5	10.0	27.7	7.43	1.33	1.44	2.17	1.11	1.13		.019	.018	
CO	$F\ ^1\Pi$?	2112	198		(404)	21.8	(0.6)	.9	.9	.7	− .5	−1.89		imag							
	$B\ ^1\Sigma$	2182	50	16.6	(43)	7.37	(2.8)	2.7	2.5	2.9	− 19.1	−23.4	1.63	imag	imag	1.118		.028	.042	.042	
	$A\ ^1\Pi$	1516.7	17.24	17.2	26.7	2.11	2.0	4.6	3.1	4.1	11.2	3.95	1.35	1.46	2.37	1.232	1.23	.024	.024	.023	
	$a'\ ^3\Sigma$?	1182	9		9.0	.39	3.9	15.0	4.0	4.8	25.6	1.66					1.38				
	$a\ ^3\Pi$	1739.3	14.5	15.3	17.1	1.55	4.0	8.2	4.8	6.4	17.6	4.54	1.35	1.45	2.11	1.202	1.21	.02	.020	.019	9
	$X\ ^1\Sigma^+$	2169.32	13.278	15.4	11.1	1.30	10.0	15.2	8.2	10.9	30.9	6.68	1.33	1.44	2.07	1.127	1.14	.01738	.018	.017	10

TABLE I. (*Continued.*)

TABLE I. (*Continued.*)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
FORMULA	STATE	ω_e EXP.	$\omega_e x_e$ EXP.	$\omega_e x_e$ CALC. FROM r_e ($a=6$)	$\omega_e x_e$ CALC. FROM D_e ($a=4$)	a' FROM $\omega_e z_e$ ($a=6$)	D_e EXP.	$(C'-C)$ FROM $\omega_e x_e$ ($a=6$)	$(C'-C)$ 0.8 FROM $\omega_e x_e$ ($a=4$)	D_e FROM MORSE'S EQUATION	C' FROM $\omega_e x_e$ ($a=6$)	C FROM $\omega_e x_e$ ($a=6$)	r_{12} FROM $\omega_e x_e$ ($a=7$)	r_{12} FROM $\omega_e x_e$ ($a=6$)	r_{12} FROM $\omega_e x_e$ ($a=4$)	r_e EXP.	r_e FROM $r_{12}=1.46$ ($a=6$)	α EXP.	α FROM $\omega_e x_e$ ($a=6$)	α FROM MORSE'S EQUATION	REF.[1]
		(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	($10^8 cm^{-1}$)	(e.v.)	(e.v.)	(e.v.)	(e.v.)	(10^{-12} erg)	(10^{-12} erg)	(10^{-8} cm)	(10^{-8} cm)	(10^{-8} cm)	(10^{-8} cm)	(10^{-8} cm)	(cm^{-1})	(cm^{-1})	(cm^{-1})	
NO	$D\ ^2\Sigma^+$	2351	27		(13)	4.28	(9.5)	5.9	4.8	6.3	32.9	23.5					.93					
	$C\ ^2\Sigma^+$	2355	15.8	15.9	(13)	2.10	(9.5)	12.1	7.9	10.8	29.5	10.31	1.33	1.46	2.56	1.07	1.07		.018	.018	11
	$B\ ^2\Pi_{reg}$	1038.6	7.46	7.1	(9)	.19	(2.89)	26.6	3.9	4.5	43.7	1.35	1.40	1.46	1.80	1.413	1.41	.015	.014	.012	12
	$A\ ^2\Sigma^+$	2375.3	16.52	16.7	(13)	2.25	(10)	11.4	7.5	10.5	29.1	10.92	1.33	1.46	imag	1.060	1.06	.016	.019	.019	
	$X\ ^2\Pi_{irreg}$	1906.5	14.44	15.3	(14)	1.80	(6.1)	9.2	5.7	7.7	21.0	6.29	1.34	1.45	2.24	1.146	1.15	.0182	.018	.018	12
BeF	$A\ ^2\Pi_{reg}$	1172.6	8.78	11.2	(16)	.11	(1.9)	46.9	4.3	4.8	75.9	1.39	1.38	1.45	1.78	1.390	1.40	.01610	.019	.015	
	$X\ ^2\Sigma^+$	1265.6	9.12	12.5	(8)	.18	(6.0)	33.4	4.7	5.4	54.6	1.64	1.34	1.44	1.80	1.357	1.38	.01685	.019	.016	

[1] Except as otherwise noted, the experimental data are from W. Jevons, *Report on Band Spectra of Diatomic Molecules*, The University Press, Cambridge, England, 1932.
[2] D. Coster and H. H. Brons, Zeits. f. Physik **73**, 747 (1932).
[3] W. W. Watson and P. G. Koontz, Phys. Rev. **46**, 32 (1934). For the first N_2^+ state listed, $r_e=1.16$A was assumed in calculating the values of α.
[4] S. M. Naude, Proc. Roy. Soc. **A136**, 114 (1932).
[5] H. G. Gale and G. S. Monk, Astrophys. J. **69**, 77 (1929). $\omega_e x_e$ was assumed to be equal to $\omega_0 x_0$ and ω_e to $\omega_0+\omega_0 x_0$. If $\omega_e y_e$ is large, as indicated by the calculated values for the $^1\Sigma$ state, the ω_e and $\omega_e x_e$ values given (and also other quantities derived therefrom) are not accurate. The "experimental" r_e value for this state was calculated from Be and the value of α in col. 20. $r_0=1.48$A.
[6] H. Barwald, G. Herzberg and L. Herzberg, Ann. d. Physik **20**, 569 (1934), give 4.8, 6.8 and 9.7 electron volts, respectively, for D_e for the 3 states of CN listed.
[7] L. Herzberg, Zeits. f. Physik **84**, 571 (1933).
[8] F. A. Jenkins and A. McKellar, Phys. Rev. **42**, 464 (1932).
[9] G. H. Dieke and J. W. Mauchly, Phys. Rev. **43**, 12 (1933).
[10] D. N. Read, Phys. Rev. **46**, 571 (1934).
[11] As a first approximation, $B_e\approx B_0=1.955$, $r_e\approx r_0=1.072$, and $\omega_e\approx\omega_1=2347$. By Eqs. (27), (28) and (29), $\omega_e x_e\approx 15.74$. Using (30), $\omega_e\approx 2355$. Recalculation of $\omega_e x_e$ by Eqs. (27), (28) and (29) then gives 15.64. By means of Eqs. (15) and (21), $\alpha\approx 0.0183$, from which $B_e=1.964$ and $r_e=1.071$. Using this r_e then gives $\omega_e x_e=15.77$, from which $\alpha=0.0185$.
[12] The values given are averages for the doublets.

The constant c is arbitrary; in this paper it will be taken as 10^{-12} erg, the value used for the alkali halide crystals. The distances r, r_e, r_0 and r_{12} will be measured in Angstrom units and a and a' in reciprocal Angstroms (10^8 cm^{-1}).

We shall consider in this paper only diatomic molecules composed of elements in the first row of the periodic table, and except from consideration the Li_2 molecule, since it contains a much smaller number of electrons than the others for which data are available.

From the band spectrum constants ω_e, $\omega_e x_e$, r_e and α rough values of a can (in most cases) be calculated. For the molecules being considered a is usually about 6. For any assumed value of a, all the other constants a', C', C and r_{12} are obtainable from ω_e, $\omega_e x_e$ and r_e.

The assumption that a is exactly 6 in all cases leads to approximately the same value of r_{12}, not only for different electronic states of the same molecule but also for different molecules. (See col. 15, Table I.) In the highest energy state of each molecule for which data are available, the calculated r_{12} values are usually higher than for the lower energy states. All values of r_{12} for the C_2 molecule are also a little high, perhaps on account of the smaller number of electrons. Otherwise, in all cases but one for which data are available, the calculated r_{12} values are within 0.02A of 1.46A. This means that, to this same degree of approximation, the r_e values can be calculated from ω_e and $\omega_e x_e$, assuming exactly the same repulsive term for all of these molecules in all but highly excited states. (See cols. 17 and 18.)

Calculations of $\omega_e y_e$ and $\omega_e z_e$ show them to be small in all cases. The agreement with experiment is apparently as good as with Morse's equation (giving $\omega_e y_e=\omega_e z_e=0$) but still not good in the cases where the experimental constants are large. This probably means that this form of potential function, like Morse's, is not a very good approximation for large values of r.

Further evidence to the same effect is afforded by the fact that the values of $C'-C$ do not agree well with the values of dissociation energy (col. 8) where the latter are known. Better agreement is obtained using $a=4.0$ and the empirical relationship

$$D_e=0.8(C'-C), \tag{6}$$

the quantity in parenthesis being calculated with the a value just mentioned, is fairly accurate (col. 10). D_e values calculated in this way are as a rule more accurate than those calculated by means of Morse's equation (col. 11).

Calculation of the rotational constant α gives practically the same degree of agreement with the experimental values as obtained from Morse's equation (cols. 19, 20 and 21).

Rough values of $\omega_e x_e$ are obtainable from ω_1, r_e or r_0 and the assumption that $r_{12}=1.46$A, with $a=6.0$ (col. 5).

Calculation of a', C and C' from ω_e, $\omega_e x_e$ and a

Expanding the exponentials of Eq. (1) and collecting corresponding terms, one obtains an equation of the form[4]

$$U=E_e+c_2(r-r_e)^2+c_3(r-r_e)^3+c_4(r-r_e)^4+\cdots \quad (7)$$

with
$$c_2=aC(a-a')/2=aa'(C'-C)/2, \quad (8a)$$
$$c_3=-aC(a^2-a'^2)/2\cdot 3, \quad (8b)$$
$$c_4=aC(a^3-a'^3)/2\cdot 3\cdot 4, \quad \text{etc.} \quad (8c)$$

The values of c_2, c_3 and c_4 are given in terms of the band spectrum constants by the equations[5]

$$c_2=2\pi^2c^2\omega_e^2\mu, \quad (9a)$$
$$\omega_e=(c_2/2\pi^2c^2\mu)^{\frac{1}{2}}, \quad (9b)$$
$$c_3=-(c_2/r_e)(\alpha\omega_e/6B_e^2+1), \quad (10a)$$
$$\alpha=-(c_3r_e/c_2+1)(6B_e^2/\omega_e), \quad (10b)$$
$$c_4=5c_3^2/4c_2-2\omega_e x_e c_2/3B_e r_e^2, \quad (11a)$$
$$\omega_e x_e=(15c_3^2/8c_2^2-3c_4/2c_2)B_e r_e^2. \quad (11b)$$

Substituting Eqs. (8a) and (8b) in Eq. (11b),

$$\omega_e x_e=(1/24)(2a^2+7aa'+2a'^2)B_e r_e^2, \quad (12)$$
$$a'=(33a^2/16+12\omega_e x_e/B_e r_e^2)^{\frac{1}{2}}-7a/4. \quad (13)$$

Since
$$B_e r_e^2=10^{16}h/8\pi^2c\mu=16.78/M \quad (14)$$

where M is the reduced mass in atomic weight units

$$a'=(33a^2/16+96\pi^2c\mu\omega_e x_e/10^{16}h)^{\frac{1}{2}}-7a/4$$
$$=(2.0625a^2-0.7154M\omega_e x_e)^{\frac{1}{2}}-1.7500a. \quad (15)$$

[4] Jevons, reference 1, Table I, p. 23.

[5] Jevons, reference 4, p. 27. The additional correction terms in the corresponding equations derived by J. L. Dunham, Phys. Rev. **41**, 721 (1932) are of negligible magnitude.

Curves showing the variation of a' with $M\omega_e x_e$ for $a=6.0$ and 4.0 are shown in Fig. 1.

From Eqs. (8a), (9a) and (15) we obtain (in 10^{-16} erg)

$$(C'-C)=\frac{2c_2}{aa'}=\frac{4\pi^2c^2\mu\omega_e^2}{aa'}=\frac{0.0585M\omega_e^2}{aa'}$$

$$=\frac{0.0585M\omega_e^2}{(33a^2/16+12\omega_e x_e/B_e r_e^2)^{\frac{1}{2}}a-7a^2/4}. \quad (16)$$

From Eq. 2,

$$C=(C'-C)/(a/a'-1). \quad (17)$$

C' is of course the sum of $(C'-C)$ and C. Thus, by means of Eqs. (15) and (17) we can obtain, from ω_e and $\omega_e x_e$ the constants a', C and C' for any given value of a. The calculated values for $a=6.0$ are given in columns 7, 12 and 13 of Table I.

Calculation of r_{12} and r_e

Assuming Eq. (4), with $c=10^{-12}$ erg,

$$(r_{12}-r_e)=(2.303/a)\log(10^{12}C). \quad (18)$$

The values of r_{12} computed by adding to the observed r_e values the values of $(r_{12}-r_e)$ obtained in this way are given in columns 14, 15 and 16 for $a=7.0$, 6.0 and 4.0. The constancy of the values calculated for $a=6.0$ has already been noted. Nearly as good constancy is obtained for $a=7.0$, r_{12} being then approximately 1.35A in

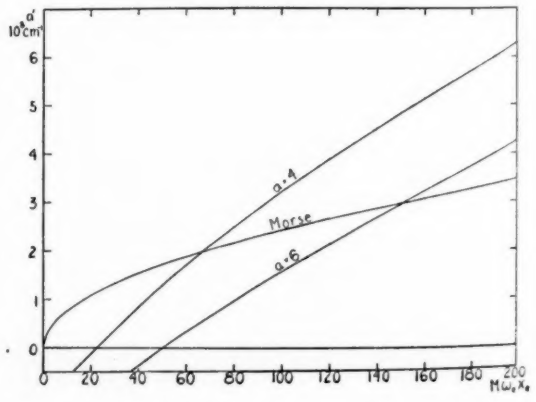

FIG. 1. The relationship between $M\omega_e x_e$ and a', for $a=4$, for $a=6$ and assuming Morse's equation.

practically all cases. Such agreement would seem to be ample evidence for the approximate constancy of the repulsive term, i.e., for the approximate correctness of Eq. (4) (at distances not far removed from r_e), with a constant value of a.

The calculated r_{12} values show a definite trend for each type of molecule, from a minimum of 1.44A or 1.45A (for $a=6.0$) for the normal state to much higher values for the higher energy states (low values of $(C'-C)$ and of D_e). For the latter the assumptions involved in Eqs. (1) and (4), with constant a and r_{12} are certainly inaccurate.

The approximate constancy of a and r_{12} for 1st row elements makes possible the calculation of r_e in cases where it is not known. To indicate the accuracy to be expected, the values in col. 18, calculated on the assumption that $a=6.0$, can be compared with the experimental values of col. 17. For states of high energy (low D_e) the calculated r_e values should be considered only as minimum values. Better agreement is of course obtained when allowance is made for the trend of r_{12} with D_e or $(C'-C)$.

Calculation of $\omega_e y_e$ and $\omega_e z_e$

To calculate $\omega_e y_e$ and $\omega_e z_e$ we may use equations derived by Dunham.[6] His constants a_1, a_2, etc., are related to those used in this paper by the equations

$$a_1/r_e=c_3/c_2=-(a+a')/3, \tag{19a}$$

$$a_2/r_e^2=c_4/c_2=a^2+aa'+a'^2/3\cdot 4, \tag{19b}$$

$$a_3/r_e^3=c_5/c_2$$

$$=-(a^3+a^2a'+aa'^2+a'^3)/3\cdot 4\cdot 5, \tag{19c}$$

$$a_n/r_e^n=c_{n+2}/c_2$$

$$=2(-1)^n(a^n+a^{n-1}a'+\cdots+a'^n)/(n+2)!. \tag{19d}$$

By using these and Eqs. (9a) and (13) one can calculate, for an assumed value of a, $\omega_e y_e$ and $\omega_e z_e$ as functions of a', M and ω_e.

Values of $\omega_e y_e$ for the molecules listed in Table I have been calculated for $a=4.0$ and $a=6.0$. In both cases they are all very small, in agreement with the usual experimental observations. In only 2 cases are the calculated values greater than 0.13 cm^{-1} for $a=6.0$ or 0.07 for $a=4.0$. Comparison with such $\omega_e y_e$ values as have been determined experimentally shows but little better agreement (if any) than is obtained with Morse's function. The assumed potential function is obviously far from accurate (at least in these cases) for interatomic distances far from r_e.

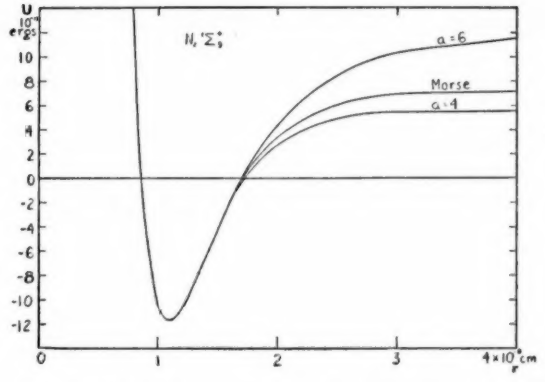

FIG. 2. Potential energy curves for the ground state of N_2, assuming $a=4$, $a=6$, and Morse's equation. These curves are all made to agree at $r=r_e$. The true curve approaches the line $U=0$ asymptotically as r approaches infinity.

Calculation of the Dissociation Energy D_e

If Eq. (1) were strictly true for all values of r, the dissociation energy D_e would be equal to $(C'-C)$. However the choice of $a=6.0$, which gives good agreement between r_{12} values for different molecules and electronic states and which we may assume gives a potential function approaching the truth quite closely for r not far from r_e, give $(C'-C)$ values which, like Morse's, are much too high. (Compare columns 8, 9 and 11 of Table I.)

An attempt was made to determine what value of a would give agreement with the otherwise determined dissociation energies, for those first row molecules for which values of the latter (not in parenthesis) are given by Jevons. Eliminating a' from Eqs. (15) and (16) one obtains

$$(2.0625a^2+0.7154M\omega_e x_e)^{\frac{1}{2}}a-1.750a^2$$

$$=0.0585M\omega_e^2/(C'-C). \tag{20}$$

Out of 10 cases, in only one is any value of a

[6] J. L. Dunham, reference 5.

possible which will satisfy this equation, using Jevons' values of D_e, ω_e and $\omega_e x_e$. In all cases, however, the closest approach to agreement is obtained with a in the neighborhood of 3.5 to 4.0. Comparison between columns 8 and 10 of Table I shows that approximately

$$D_e = 0.8(C' - C) \tag{6}$$

if $(C' - C)$ is computed on the assumption that $a = 4.0$. The average deviation (not counting the D_e values given in parenthesis by Jevons) is less than 0.7 electron volt.

Calculation of α

Eq. (10b) furnishes a method of calculating the rotational constant α. Substituting for c_2 and c_3,

$$\alpha = (2B_e^2/\omega_e)[(a + a')r_e - 3]. \tag{21}$$

The values in column 20 of Table I were calculated in this way, taking $a = 6.0$. Calculations assuming $a = 4.0$ lead to but slightly different results. The α so computed averages 0.0015 cm^{-1} less, the maximum difference being 0.004 (not counting the exceptional $^1\Sigma$ state of F_2, where the difference is 0.04 cm^{-1}). The average deviation between the observed values of α and those calculated, assuming either a value, is less than 0.003 cm^{-1}.

In the instances in which B_0 was known but not B_e, the former was used to obtain an approximate value of α; this was then employed in calculating B_e from the relation

$$B_e = B_0 + \alpha/2 \tag{22}$$

and finally a more exact value of α was computed from this B_e.

The expression for α derived by Dunham[6] leads to an equation of the form of (21) except for the addition of a complicated correction term. The magnitudes of the correction terms for the $^1\Sigma$ state of F_e and the $F\,^1\Pi$ state of CO (probably the worst cases), assuming $a = 6.0$, are about 2×10^{-5} and 10^{-6} cm^{-1}, respectively.

Assuming Morse's equation,

$$a' = a/2 = (8\pi^2 c\mu\omega_e x_e/10^{16}h)^{\frac{1}{2}}. \tag{23}$$

Substituting in Eq. (21),

$$\alpha_M = 6B_e^2/\omega_e[(8\pi^2 c\mu\omega_e x_e/10^{16}h)^{\frac{1}{2}} r_e - 1]$$
$$= 6B_e^2/\omega_e[(\omega_e x_e/B_e)^{\frac{1}{2}} - 1]. \tag{24}$$

This is equivalent to the equation

$$\alpha = 2x_e B_e[3(B_e/\omega_e x_e)^{\frac{1}{2}} - 3(B_e/\omega_e x_e)] \tag{24a}$$

derived by Pekeris.[7]

The figures (col. 21) obtained by means of Eq. (24) closely parallel those (col. 20) obtained from Eq. (21), as might be expected.

Calculation of a from α, ω_e, $\omega_e x_e$ and r_e

From Eqs. (15) and (22) one obtains

$$a + a' = \alpha\omega_e/2B_e^2 r_e + 3/r_e$$
$$= (33a^2/16 + 0.7154 M\omega_e x_e)^{\frac{1}{2}} - 3a/4. \tag{25}$$

Solving for a,

$$a = /F2 \pm (11F^2/12 - 0.4769 M\omega_e x_e)^{\frac{1}{2}}, \tag{26}$$

where
$$F = \alpha\omega_e/2B_e^2 r_e + 3/r_e. \tag{26a}$$

Calculations of a using this relationship lead to imaginary values in 10 cases out of 36 for which the data are available. Either the method is too sensitive to experimental inaccuracies or else the assumed equations are not sufficiently valid. It is perhaps significant however that the average of the 26 other cases is 6.0, the value found to give such uniform values of r_{12}, with an average deviation of 0.9.

Calculation of $\omega_e x_e$ from ω_1 and r_e

From Eq. (18) we have

$$C = 10^{-12} \log^{-1}[a(r_{12} - r_e)/2.303], \tag{27}$$

from Eqs. (16) and (17)

$$a' = a - 0.0585 M\omega_e^2/aC, \tag{28}$$

and from Eqs. (12) and (13)

$$\omega_e x_e = (1/M)(1.398a^2 + 4.89aa' + 1.398a'^2). \tag{29}$$

Assuming $a = 6.0$ and $r_{12} = 1.46$, values of $\omega_e x_e$ are readily computed by means of Eqs. (27), (28) and (29) from r_e and ω_e. As a first approximation ω_1 can be used in place of ω_e, the approxi-

[7] C. L. Pekeris, Phys. Rev. **45**, 98 (1934).

mate $\omega_e x_e$ so obtained being then used to calculate ω_e:

$$\omega_e = \omega_1 + \omega_e x_e/2. \quad (30)$$

A second approximation can then be made if desired. In most cases, however, the second approximation is only about 0.2 cm^{-1} lower than the first approximation and the calculated values are rarely that accurate. (Compare columns 4 and 5 of Table I.) They are especially inaccurate for highly excited states and for states having r_e, not very different from r_{12}.

Calculation of $\omega_e x_e$ and Other Constants from ω_1, a and $(C'-C)$

As already pointed out, $(C'-C)$ is not in general equal to the dissociation energy, for any assumed value of a. Taking $a=4.0$ however, one can obtain approximate $(C'-C)$ values by Eq. (6) and from these by Eqs. (16) and (29) $\omega_e x_e$ may be calculated. As in the computation of this quantity from ω_1 and r_e one can use ω_1 in place of ω_e for a rough calculation, later, if desired, using ω_e obtained by means of Eq. (30).

Values of $\omega_e x_e$ obtained in this way are given in col. 6 of Table I for comparison with the experimental values in col. 4.

Knowing $\omega_e x_e$ and ω_e, one can of course then calculate r_e, B_e, α, etc., assuming $a=6.0$ and $r_{12}=1.46$, if these are not already known.

Potential Curves for Large Values of r

Comparison of the experimental values of $\omega_e y_e$ and D_e with those calculated indicates a closer agreement, when r is much larger than r_e, if a is taken as 4.0 than if it is given a higher value. To obtain the equation of a potential curve conforming reasonably well to the actual curve for r large, it is suggested that one use this smaller value of a and Eqs. (6), (16) and (17) to obtain a', C and C' from the dissociation energy (if known) and ω_e (or ω_1).

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Entropy and the Absolute Rate of Chemical Reactions. II. Unimolecular Reactions

O. K. Rice and Harold Gershinowitz,[1] *Chemical Laboratories, Harvard and Princeton Universities*

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In this paper the considerations of the previous paper have been developed further and compared with the theory of reaction rates as formulated in terms of a specifically defined activated complex by Eyring. The theory has been applied to a discussion of various unimolecular reactions. A number of cases have been treated by considering the reverse bimolecular or trimolecular association and discussing the extent to which rotational degrees of freedom must be frozen out in order for the associations to occur. Other cases have been treated by the activated complex method, which involves discussion of the number of free rotations and the frequency of the vibrations in the complex. It has been shown that it is possible to account for the rates of a considerable number of unimolecular reactions by making reasonable assumptions and that there is a considerable class of unimolecular reactions which conform to what is designated as the "hypothesis of exact orientation," the only necessary assumption being that the rotational degrees of freedom of the fragments which recombine in the reverse reaction must be frozen out just sufficiently so that they correspond as regards their entropy terms to the resulting vibrational degrees of freedom of the molecule formed.

1. General Considerations

In a recent paper[2] (referred to hereafter as Part I) we have developed a method for the discussion of the rates of reactions which do not involve any change in the electronic states of the system. Since the publication of Part I, there has appeared an interesting paper by Eyring[3] in which the same problem is treated by a method which has many features in common with our procedure, though the viewpoint and the termi-

[1] Parker Traveling Fellow of Harvard University.

[2] O. K. Rice and Gershinowitz, J. Chem. Phys. **2**, 853 (1934).

[3] Eyring, J. Chem. Phys. **3**, 107 (1935).

nology are different. Before proceeding with the treatment of unimolecular reactions we shall attempt to correlate the two points of view. We shall then, in our applications, borrow freely from both of them, according to expediency, and we shall find that we are thus led to conclusions of interest.

It has been usual in the treatment of bimolecular reactions to consider a collision factor and a steric factor. If we consider a reaction of the type $M_2+M_3 \rightleftarrows M_1$, then, speaking very roughly, we may say that when association occurs the six translational degrees of freedom of M_2 and M_3 go over, on association, into three degrees of freedom of translation, two degrees of freedom of rotation, corresponding roughly to rotations about axes of the molecule M_1 perpendicular to the bond of M_1 which breaks in the reverse reaction, and one degree of freedom of vibration, which may be roughly described as being directed along the bond which breaks. The "A-factor" for the rates of reaction of the unimolecular reaction[4] were considered in Part I to be broken into two factors. If A_1 is the "A-factor" for the unimolecular reaction and A_2 for the bimolecular reaction, then we write

$$A_1=A_1'A_1'', \quad \text{and} \quad A_2=A_2'A_2'', \tag{1}$$

where A_1' and A_2', the "collision factors," contain entropy terms which have to do only with the above-mentioned degrees of freedom, while A_1'' and A_2'' take into account the effect of the other degrees of freedom. We finally arrived at the following expressions for A_1' and A_2':

$$A_1'=ekT/hE_1', \tag{2a}$$

$$A_2'=e(B_1C_1'/B_2B_3)kT/h. \tag{2b}$$

In expressions of this sort we mean by the B's, C's and E's antilogarithms of entropy terms for translation, rotation and vibration, respectively, the subscripts indicating the particular molecule. These antilogarithms are subsequently referred to simply as entropy factors. If a letter is unprimed, it includes all of the degrees of freedom of the particular kind which occur in the whole molecule. Primes (single or double, respectively) indicate that only those degrees of freedom which occur in the collision factor, or only those which occur in the steric factor, are to be included. The number of degrees of freedom to be included in any given entropy factor is generally easily seen and the B's, C's and E's may be evaluated from expressions like Eqs. (5), (6) and (7) of Part I. In particular, we may note that

$$E_1'=x(e^x-1)^{-1}-\ln(1-e^{-x}),$$

where $x=h\nu_1/kT$, in which ν_1 is the frequency of the vibration along the bond which breaks in the unimolecular reaction.

For the "steric factors," A_1'' and A_2'', we set down in Part I (Eqs. (11)) the following *provisional* expressions (we again use the symbol $\doteq$ to mean "equals provisionally"):

$$A_1'' \doteq (C_1''E_1'')^{-1}, \tag{3a}$$

$$A_2'' \doteq (C_2E_2C_3E_3)^{-1}. \tag{3b}$$

These provisional expressions are based on the assumption that, for the degrees of freedom involved, only one quantum state is available for reaction;[5] in other words, all these degrees of freedom must be completely frozen out in order for reaction to occur. Since this is obviously too stringent a condition on these degrees of freedom we must correct (3a) and (3b) by such entropy factors as will account for the number of states actually available for reaction. Now the vibrations of M_2 and M_3 on combination will go over into vibrations of M_1 with approximately the

[4] The rate of reaction for the unimolecular reaction is written in the form $A_1 \exp(-\epsilon_a/kT)$, where ϵ_a is the energy of activation according to the definition of Tolman (*Statistical Mechanics* (Chemical Catalog Co., 1927), p. 261–2). This is the value obtained by plotting the logarithm of the rate constant against the reciprocal of the absolute temperature. The theoretical value of A_1 is not independent of temperature but may, for comparison with experiment, be evaluated for the middle of the experimental range of temperatures, as noted in the following paper.

[5] They do assume that, if there is spin degeneracy in the electronic and nuclear states, all these degenerate states are equally available for reaction, and that the degeneracy is the same for M_1 and for the system M_2 plus M_3. This may not always be true but we may in general assume that spin does not affect the probability of a decomposition, so that (3a) will always hold. As noted in footnote 13 of Part I, however, the spin state may affect the possibility of association, since the relative orientations of the spins of M_2 and M_3 will determine whether they will attract or repel each other. So, in general, if the association involves free radicals, or systems not in S states, (3b) will not hold, but needs to be multiplied by a constant factor. This, however, will not affect considerations of the present paper, as we are interested in the unimolecular decomposition, to which (3a) applies.

same entropy. If we make the usual assumption that all vibrational states of M_2 and M_3 are equally available for reaction, we multiply (3a) and (3b) through by E_2E_3 which will approximately cancel part of E_1''. Some of the rotations of M_2 and M_3 correspond to free rotations within M_1 or to the rotation of M_1 about an axis approximately parallel to the bond which breaks; these rotations of M_1 are included in C_1''. It is reasonable to suppose that all states of these rotations of M_2 and M_3 are equally available for reaction and that the entropy expressions approximately cancel C_1'', when (3a) is multiplied through by the proper factor. The other rotations of M_2 and M_3 go over into vibrations of M_1 and one cannot say *a priori* to what extent these rotations will have to be frozen out in order for reaction to occur, but it is reasonable to suppose that they will not have to be frozen out beyond what corresponds to the entropy of the vibrations which they are going to form[6] and this is what we shall mean, hereafter, by saying that certain rotations are frozen out. Under these circumstances we must multiply (3a) and (3b) by a factor which will just cancel the remaining portions of E_1'' and we get, approximately at least,

$$A_1''=1. \tag{4}$$

Eq. (4) may be said to be the condition for the greatest possible freezing out of rotations of M_1 and M_2 (hereafter described as "exact orientation"). It is to be noted that this is what follows from the assumption that *all* states included in A_1'' are equally available for decomposition of M_1. As might be expected, under these conditions the expression for the rate reduces essentially to that obtained by Rodebush.[7]

If not all rotations have to be frozen out we get the more general expression

$$A_1''=C_2'''C_3'''/E_1''', \tag{5}$$

where C_2''' and C_3''' represent the entropy expressions for those rotations which are not frozen out and E_1''' the entropy expression for the corresponding vibrations. Of course, this is an idealized expression and varying extents of freezing out of the rotations may be necessary for reaction.

Certain considerations, to be discussed below in connection with our treatment of the alkyl azo-compounds, lead us to believe that when these compounds decompose the two alkyl groups leave the nitrogens simultaneously. This leads us to inquire as to the formulation of our theory for the case where the reverse reaction is trimolecular. Another type of trimolecular reaction has already been considered by Gershinowitz and Eyring[8] and, as a matter of fact, no new principles beyond what have been discussed above are required.

To fix the ideas we shall consider specifically the case of azomethane, as generalization to other cases, particularly the other azo-compounds, is readily made. We start with the same provisional equation for the unimolecular decomposition,

$$A_1\doteq(B_1C_1E_1)^{-1}kT/h \tag{6}$$

that was used in Part I (Eq. (9a)), collision and steric factors being included together. In the unimolecular reaction we must in this situation have three translational degrees of freedom, two rotational, and *four* vibrational going over into *nine*[9] translational degrees of freedom. It seems reasonable to include all these degrees of freedom in what may be called a collision factor. In getting the collision factor for the bimolecular reaction we assumed that in the reverse unimolecular reaction all states of the rotational degrees of freedom included in C_1' were available for reaction, and multiplied the provisional Eq. (6) through by the corresponding entropy factors. To take care of the vibration which was converted

[6] Compare Part I, p. 860.

[7] Rodebush, J. Chem. Phys. **1**, 440 (1933). If $kT\gg h\nu_1$ then in the case of exact orientation A_1 becomes equal to ν_1, in which case it is like Rodebush's expression. A similar result was also obtained by Polanyi and Wigner, Zeits. f. physik. Chemie, Haber Band, 439 (1928). The latter authors also gave a comparison of experiment and theory. In the following pages we shall give a more detailed comparison of the theory with a number of gas phase unimolecular reactions. See also Rodebush, J. Am. Chem. Soc. **45**, 606 (1923).

[8] Gershinowitz and Eyring, submitted to J. Am. Chem. Soc.

[9] Two of these vibrational degrees of freedom are the carbon-nitrogen stretching vibrations, while two will be bending vibrations of the carbon-nitrogen skeleton. Of the degrees of freedom not included in the collision factor, the rotations of the methyl group will correspond in part to free rotations in the azomethane molecule and in part to carbon-hydrogen bending vibrations, while corresponding to the rotation of the nitrogen will be the other skeletal bending vibration and the rotation about the long axis of the kinked chain.

into a translation we multiplied through by e. In this case we multiply through by the entropy factors for the two rotations and for three of the vibrations; the fourth vibration (one of the valence vibrations of the row of two carbon and two nitrogen atoms) we again take care of by multiplying through by e. The fact, that in this case some of the entropy factors by which we multiply our expression go with vibrations rather than rotations, corresponds to the necessity that in an effective triple collision there be a pretty exact lining up of the molecules; some of the translations must be frozen out to vibrations rather than merely to rotations. Only one of the vibrations is taken care of by the factor, e, because, although two bonds are broken, the two alkyl groups must leave together, since the breaking of the bonds is presumably accompanied by a simultaneous rearrangement of the nitrogen to give a triple bond, it being this rearrangement which allows the breaking of the *two* bonds with an activation energy of only 40,000–50,000 calories. As the motion of one of the alkyls is thus definitely related to that of the other, only one "normal" coordinate is actually connected with the breaking of the bond.

The result of the above considerations is that the collision factor, for the *unimolecular* reaction comes out to have the same form as before, and is given by Eq. (2a). Likewise it may be shown that the steric factor is equal to 1 for exact orientation and otherwise is given by an equation just like Eq. (5), except that the numerator contains three factors, one for each of the combining molecules or radicals, so that we have

$$A_1'' = C_2''' C_3''' C_4''' / E_1'''. \qquad (7)$$

We thus have to consider the possibility that in the reverse of the azomethane decomposition neither of the methyl radicals has to be oriented.

So far we have examined the reaction by considering the initial and final states of the system. Sometimes it is better to investigate the state of an intermediate condition, an "activation complex." Such a procedure was used in Part I in the discussion of the ethylene-hydrogen reaction and has been formulated more definitely and generally by Eyring. If we consider the system to be represented by a phase point (in the coordinate space) traveling along a potential energy surface, then, in general, reaction may be said to take place when the point passes over a saddle point on the potential energy surface. Eyring defines the "activated complex" as the state of the system just at the top of the saddle point. The activated complex differs from the molecule M_1 and also from the pair of molecules M_2 and M_3 and, in general, we may expect its properties to be intermediate between the properties of the two systems, M_1 and M_2+M_3. Rotations of M_2 and M_3 which are going to be frozen out on association will presumably have already become vibrations but these vibrations will be expected to be of very low frequency so that their entropy factors will be of the same order of magnitude as those of rotations. Looking at the situation from the point of view of the reverse reaction this would mean that certain of the vibrations of M_1 have to all intents and purposes become rotations in the activated complex. To calculate the rate of reaction one calculates the equilibrium concentration of the activated complex and multiplies by the proper absolute time factor. This may be done by multiplying the provisional rates of reaction of Part I (Eqs. (9)) by the proper entropy factors for the activation complex, such entropy factors being set up on the theoretically unjustifiable but probably practically justifiable assumption that normal coordinates for the activation complex can be found.

The method of the activated complex assumes that equilibrium is completely established all along the path as the system approaches the activated state. It may be, however, if the reaction is proceeding in that direction in which degrees of freedom are becoming loosened or "melting" that equilibrium will not be established in these degrees of freedom clear to the top point of the saddle; then the activation complex will be the system at the last point where equilibrium is established (this, of course, being an approximate statement, based on the assumption that this "last point" may be definitely defined). If this is true, then in the reverse reaction, in which degrees of freedom are being frozen out, some systems will cross over the saddle and later be forced back because of the action of the other degrees of freedom. This may really mean that the potential energy surface is more complicated than a simple saddle, which would not be sur-

prising, since it is a multidimensional affair. It might be possible to effect such a change of variables that the activation complex could always be located at the top of a saddle, but the situation defies visualization. In any event, we can treat Eyring's definition of the activated complex, which has the advantage of definiteness and concreteness, as the norm from which an activated complex in nature may differ by much or little. Whether it is advantageous to use the idea of the activated complex or not will depend in large degree on how closely the actual case conforms to this normal definition of the complex.

One case in which we believe it advantageous to use the concept of freezing out of degrees of freedom rather than the concept of the activated complex is the case of exact orientation, discussed above, a case which we shall see seems to be frequently realized experimentally. From the activated complex point of view exact orientation follows if the activated complex has the same frequencies and moments of inertia as the molecule M_1, except in the degree of freedom in which dissociation is taking place. It seems likely, however, if we insist on the normal definition of an activated complex, that we should actually expect the complex to be much more loosely bound than this would indicate. Furthermore, this case often occurs when we should expect the activation energy of the bimolecular association to be zero. If this is true, the height and position of the saddle point may depend strongly on the angular momentum of M_1 and M_2 with respect to each other, which complicates the situation. In this case, the concept of the freezing out of degrees of freedom therefore seems preferable.

On the other hand, in cases where the degrees of the freedom before and after reaction are not easily correlated, it may be necessary to consider some kind of a complex. This we found to be the case in the ethylene-hydrogen reaction and it is necessary in the study of bimolecular and trimolecular reactions, which are not associations. In the case of some of the unimolecular reactions which we shall treat below, namely the decompositions of the tertiary alcohols, the isomerization of cyclopropane and the decomposition of certain esters, we have used essentially the idea of the activated complex but the two points of view are so nearly interchangeable that we use freely, in discussing the same reaction, any of the expressions, "the state of the activated complex," "the number of degrees of freedom frozen out," "the number of quantum states from which reaction can occur," etc.

2. The Decompositions of the Alkyl Iodides

Ogg[10] has found that methyl, ethyl and *n*-propyl iodides decompose in the neighborhood of 600°K according to the mechanism $RI \rightarrow R + I$, with rate constants given, respectively, by $3.93\times10^{12}\exp(-43{,}000/RT)$, $1.82\times10^{13}\exp(-43{,}000/RT)$, and $2.80\times10^{13}\exp(-43{,}000/RT)$ sec.$^{-1}$.

The evaluation of Eq. (2a), assuming that E_1' involves a frequency of the order of 500 cm^{-1}, the frequency which is associated with an iodine atom,[11] gives the same value of A_1' for all the iodides at 600°K, namely 1.45×10^{13}. This agrees within the limits of error with the experimental values of A_1 and suggests that exact orientation of the alkyl radicals is necessary for recombination. The value for methyl iodide is, indeed, a little small. It may well be that the recombination of methyl radicals and iodine atoms cannot take place at every collision because of difficulty in the transfer of translational to vibrational energy; if this be so the reverse reaction will take place correspondingly more slowly.

3. The Decomposition of Alkyl Nitrites

Steacie and Shaw[12] have studied the rates of decomposition of methyl and ethyl nitrites at around 200°C. Allowing for the fact that these reactions probably involve a chain of two,[12b] the rates for the initial process, in which, probably, an NO molecule splits off, may be written as $0.92\times10^{13}\exp(-36{,}400/RT)$ and $7.0\times10^{13}\exp(-37{,}700/RT)$ sec.$^{-1}$, respectively. Making the assumption that exact orientation is required for the reverse reaction, thus setting $A_1=A_1'$, and using Eq. (2a) (calculating E_1' from the assumption that an NO vibration of frequency near 1500

[10] Ogg, J. Am. Chem. Soc. **56**, 526 (1934).
[11] Kohlrausch, Zeitz. f. Elektrochemie. (a) **40**, 429 (1934); (b) *Der Smekal-Raman Effekt* (Springer, 1931), p. 154.
[12] (a) Steacie and Shaw, J. Chem. Phys. **2**, 345 (1934); Proc. Roy. Soc. **A146**, 388 (1934). See also (b) F. O. Rice and Rodowskas, J. Am. Chem. Soc. **57**, 350 (1935).

cm^{-1} is involved[13]) we find that A_1 for both reactions comes out to be 2.4×10^{13}. This is probably equal to the observed values within the limit of error, although the difference between values for methyl and ethyl nitrites seems rather large to be all error and it is a little difficult to account for as large a difference.

4. The Decomposition of the Tertiary Alcohols

The splitting off of water from tertiary butyl and tertiary amyl alcohols has been studied by Schultz and Kistiakowsky,[14] who find the reaction rates to be given by $4.8\times10^{14}\exp(-65{,}500/RT)$ and $3.3\times10^{13}\exp(-60{,}000/RT)$ $sec.^{-1}$ at around 500°C. In this case we may assume that the primary reaction involves a shift of a hydrogen atom from a carbon atom to the oxygen. Such a reaction involves, essentially, the breaking of a bond, but not the formation of two separate bodies, at least in the primary reaction. If we start with the provisional Eq. (6) and assume that all the translational, vibrational and rotational levels are equally available for reaction, except that the vibration directly connected with the bond which breaks is to be taken care of in the usual way by multiplication by e, we get for the case of the tertiary butyl alcohol $A_1=3A_1'$ where A_1' is given by Eq. (2a), the term E_1' involving a single carbon hydrogen stretching vibration of about[11] 3000 cm^{-1}. The factor 3 is introduced because there are three methyl radicals which can give a hydrogen to the oxygen, it being assumed that one of the hydrogens on any given methyl is always in a position where it can go over to the oxygen and that the hydrogen on the oxygen does not get in the way. It might, perhaps, be expected that there should be some freezing out of the rotations of the methyl and the hydroxyl radicals but, on the other hand, it might well be that this would be unnecessary if there were a small amount of energy of activation in other degrees of freedom than the particular one which "breaks." In any event, on the basis of these assumptions, we find $A_1=1.2\times10^{14}$ which is still somewhat less than the experimental value, but the greater experimental value may be due to some loosening of the bending vibrations of the active hydrogen when it is in the activated condition.

The case of tertiary amyl alcohol is somewhat different, inasmuch as the end hydrogens of the ethyl group are differently situated than the others. It is possible for them to come closer to the oxygen than the other hydrogens and this probably accounts for the lower activation energy and higher overall reaction rate.[14a] The fact that the A_1 value is lower is probably due to the fact that there is free rotation of the ethyl radical and that this free rotation has to be frozen out in the most favorable position for reaction to take place. If this degree of freedom has to be completely frozen out the value of the A_1 factor for the reaction of these hydrogens would be about 90-fold smaller than the value for reaction from a single methyl radical, namely $4.0\times10^{13}/90$ or 4.4×10^{11}. The actual value with which this is to be compared is not the experimental value for t-amyl alcohol. We must rather take the experimental rate constants for t-amyl alcohol and subtract from them 8/9 of the values of the rate constants for t-butyl alcohol (t-amyl alcohol has 8 hydrogens in positions similar to the 9 hydrogens on the methyl groups of t-butyl alcohol). An approximate result is obtained if we note that around the middle of the range of temperatures over which t-amyl alcohol was investigated 8/9 of the rate of decomposition of t-butyl alcohol constitutes about 38 percent of the rate of decomposition of t-amyl alcohol. We may therefore conjecture that the true energy of activation of the part of t-amyl alcohol decomposition which we are interested in should differ 38/62 more from the energy of activation of t-butyl alcohol than the observed difference. This lowers the activation energy by 3400 calories and will make the true value of A_1 become $3.3\times10^{13}\times0.62\times\exp(-3400/RT)=2.3\times10^{12}$. This is somewhat larger than calculated but this is not unexpected inasmuch as complete freezing out of the rotation of the ethyl radical should not be necessary for reaction. Although the calculations agree reasonably well with the experimental results in this case, per-

[13] Kohlrausch, reference 11b, p. 188.

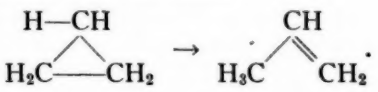
[14] Schultz and Kistiakowsky, J. Am. Chem. Soc. **56**, 395 (1934).

[14a] The mechanism assumed here implies either the immediately subsequent shift of a second hydrogen atom or the formation of dimethyl cyclopropane. It would thus be of interest to ascertain whether any of the latter substance were present in the reaction products.

haps too much emphasis should not be placed on this fact, on account of the possibility of fairly large errors in the activation energies. We have felt however, that the above calculations should be presented as they may serve as predictions of what may be expected to occur in the splitting out of HCl from tertiary chlorides. Such reactions are now being studied by Kistiakowsky and Brearley.

5. The Isomerization of Cyclopropane

This reaction has been studied around 500°C by Chambers and Kistiakowsky[15] who find for the rate constant $1.48\times10^{15}\exp(-65{,}000/RT)$ sec.$^{-1}$. Chambers and Kistiakowsky have discussed two possible mechanisms for this reaction. The first mechanism involves the breaking of a carbon-carbon bond and a subsequent rearrangement, consisting in the shift of a hydrogen atom. Although the reverse of this reaction is not an association, but another unimolecular reaction, we should expect it to proceed like a reaction requiring exact orientation; if, namely, we make the assumption that all states of the molecule are equally available for reaction we see that A_1 should be equal to $3A_1'$ as given by Eq. (2a) with ν_1' equal to 1000 cm^{-1}, the frequency of a carbon-carbon stretching vibration,[11] the factor 3 being introduced because there are three bonds which can break. This yields $A_1=8.1\times10^{13}$ and it is seen that it is much too small. Chambers and Kistiakowsky also suggested that the mechanism might consist in the jumping of a hydrogen from one carbon to an adjacent one with simultaneous formation of a double bond,



In this case, we naturally assume that A_1 is equal to $12A_1'$, as given by Eq. (2a), with ν_1' equal to a carbon-hydrogen frequency, the factor 12 being introduced because there are six hydrogen atoms and each one can go to either of two carbon atoms. It is not certain whether this would be a stretching or bending[16] frequency; we assume it to be the latter, which can only cause A_1 to have too small a value. This assumption gives $A_1=3.9\times10^{14}$, probably agreeing with experiment within the limit of error; in any event, the difference could easily be accounted for by a slight loosening of the frequencies in the activation complex. This, we believe, is evidence in favor of the hydrogen shift mechanism, though one must be cautious in drawing conclusions on the basis of such grounds as these. It may be well to remark that one cannot exclude the assumption that a carbon-carbon bond breaks first, equilibrium being established between the activated molecules thus formed and the normal molecules, and that the subsequent rearrangement is the rate determining step. At first sight it would appear that the rate for this mechanism would be too large, for one would naturally assume that the intermediate would have free rotations, which would mean that its entropy would be large and its concentration correspondingly great. However, if these free rotations must be frozen out again before the rearrangement can take place, the same rate will result as with the direct shift of the hydrogen. With this condition imposed the difference between the two mechanisms in which the hydrogen shift is the rate-determining step becomes in a sense trivial.

Assuming that the rate-determining step is the shift of a hydrogen atom, it will be of interest to consider the reverse reaction, namely, the formation of cyclopropane from propylene. In propylene a free rotation of a methyl group with entropy term C_2'', let us say, takes the place of a carbon-hydrogen bending vibration with entropy factor E_1'', while a rotational entropy factor C_2' takes the place of the rotational entropy factor C_1 of the cyclopropane. We shall neglect changes in the vibrational frequencies and assume that $C_2'/C_1=6$, since 6 is the symmetry number of cyclopropane. A consideration of the relation between rate constants of direct and reverse reactions and equilibrium constant then shows us at once that the relation between A_2, the "A-factor" for the *propylene* isomerization, and the factor A_1 for isopropane should be given by

$$A_2/A_1=(C_1/C_2')(E_1''/C_2'')=E_1''/6C_2''.$$

Suppose now that we should assume that in the isomerization of propylene one of the hydrogen

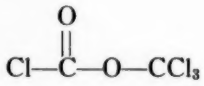
[15] Chambers and Kistiakowsky, J. Am. Chem. Soc. **56**, 399 (1934).

[16] Kohlrausch, reference 11a, and reference 11b, p. 206.

atoms on the methyl group is always in a position to react, as we have done in the decomposition of the tertiary alcohols; suppose, in fact, that all states of the molecule are equally available for reaction; we then find that A_2 will be given by an expression like (2a), namely ekT/hE_2', where E_2' involves, probably, a carbon-hydrogen bending vibration. But we have already assumed $A_1 = 12ekT/hE_1'$ where $E_1' = E_2'$. Hence we should have $A_2/A_1 = E_1''/6C_2'' = 1/12$, or $E_1''/C_2'' = 1/2$. Actual calculation of E_1''/C_2'' (remembering that the free rotation of a methyl involves a symmetry number of 3) gives 0.14. This shows that the assumptions we have made regarding A_1 and A_2 are not quite consistent with each other (and as cyclopropane is undoubtedly a stiffer structure than propylene the discrepancy is actually a little greater than this). In view of the roughly approximate nature of these considerations such a difference is not unexpected. Assuming that the estimate of A_2 is correct, we get for A_1 the value 1.5×10^{15}, a result which is in closer agreement with experiment than the value originally obtained.

6. The Decomposition of Trichloromethyl Chloroformate

The decomposition of trichloromethyl chloroformate,



to give two molecules of phosgene, which according to Ramsperger and Waddington[17] has a rate constant given by $1.4\times10^{13}\exp(-41{,}500/RT)$ sec.$^{-1}$ at around 300°C, is undoubtedly similar to the isomerization of cyclopropane, inasmuch as it must involve the transfer of a chlorine atom from one carbon atom to the other. While the O—C Cl_3 group can presumably rotate freely about the other carbon-oxygen bond this will not change the relative position of the chlorines with respect to the other carbon atom and if we assume that one chlorine is always in a position to react, then the reaction consists essentially in the breaking of a carbon-chlorine bond, followed by the breaking of a carbon-oxygen bond, and the formation of another carbon-chlorine bond. In the latter processes some vibrational frequencies change to rotational but it seems reasonable to suppose that these rotational frequencies would have to be frozen out for recombination to occur. If we assume that the breaking of the carbon-chlorine bond is the rate determining step, which seems likely, as it would appear that the chlorine is the active atom in the decomposition, then A_1 should be equal to A_1', as given by Eq. (2a), with E_1' calculated on the assumption that it involves a carbon-chlorine stretching frequency of about[11] 700 cm^{-1}. The value of A_1 thus obtained is 1.9×10^{13}, in good agreement with the experimental value.

7. The Decompositions of Certain Esters

Coffin[18] has studied the decompositions of ethylidene diacetate, ethylidene dipropionate and butylidene diacetate at temperatures somewhat above 200°C and found the A_1 factors to be, respectively, 2.0×10^{10}, 2.5×10^{10} and 3.2×10^{10}. Contrasted to the values generally obtained from the hypothesis of exact orientation, $2-3\times10^{13}$, these seem at first sight very low. However, it seems probable that the reaction goes, as shown in Fig. 1, through an activated complex in which three degrees of freedom of free rotation which can normally occur in the ester (about three of the bonds shown dotted in the activated complex) have become frozen out into vibrations. As we have stated above, the hypothesis of exact orientation gives the same result as assuming that, except for the bond that breaks, the activated complex is entirely similar to the decomposing molecule; in this case, in which three rotational degrees of freedom have become vibrations in the complex, the result will be obtained by multiplying the rate to be expected for exact orientation by E_0/C_1''' where E_0 is the entropy expression for the vibrations in the complex and C_1''' is the entropy expression for the rotations frozen out. Now it is very difficult to make an estimate of C_1''' for these cases, as we do not know enough about the dynamics of such complicated molecules. It is obvious, however, that the moments of inertia involved will be large and a rough estimate for ethylidene diacetate indicates

[17] Ramsperger and Waddington, J. Am. Chem. Soc. **55**, 214 (1933).

[18] Coffin, Can. J. Research **5**, 636 (1931); **6**, 417 (1932).

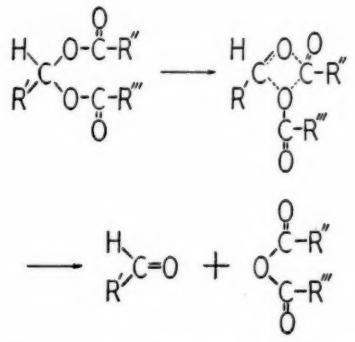


FIG. 1. The decomposition of esters like ethylidene diacetate. *Erratum:* An H—C and an R′—C bonding line were unintentionally omitted in the activated complex.

C_1''' will probably be of the order of 10^6. Since E_0/C_1''' must be of the order of 10^{-3}, we see that E_0 must be around 10^3, which would make the vibrations involved of the order of 90 to 100 cm^{-1}. Since the complex is undoubtedly very loosely bound and 100 cm^{-1} is not far below the lower bending frequencies in complex molecules, this does not seem at all unreasonable. As the moments of inertia of the other esters are undoubtedly larger than those for ethylidene diacetate it might be expected that the A_1's would decrease rather than increase, but it is also very probable that in these cases the complex would have still lower frequencies, which might about cancel the other effect.

8. The Decompositions of the Azo-Compounds

We shall next consider the decompositions of azomethane[19] and azoisopropane,[20] which go in the neighborhood of 570°K. The respective rate constants are given[21] by $3.1\times10^{16}\exp(-52{,}440/RT)$ and $5.7\times10^{13}\exp(-40{,}900/RT)$ $sec.^{-1}$.

Assuming that the frequency involved in Eq. (2a) is of the order of magnitude of carbon-nitrogen stretching vibrations, namely[22] 1000 cm^{-1}, we get $A_1=2.4\times10^{13}$ for both azomethane and azoisopropane if we use the hypothesis of exact orientation. This agrees within the limits of error with azoisopropane.

The rate of reaction of azomethane, however, is much faster than we would expect from the hypothesis of exact orientation. Let us, therefore, attempt to calculate A_1'' from Eq. (5), assuming that the methyl radical on combination with the $CH_3-N=N-$ radical, does not need to be oriented at all. The moments of inertia of the methyl radical (assuming tetrahedral angles are preserved and that the carbon atom is at the center of gravity) are 5.17×10^{-40} and 3.24×10^{-40}, the latter representing two degrees of freedom. The entropy term corresponding to the larger of the above moments is the one which will cancel against the entropy due to the free rotation of the methyl radical in azomethane. We can, therefore, write in this case

$$A_1''=\pi^{-1}(8\pi^3eI'''kT/h^2)/E_1''',$$

where $I'''=3.24\times10^{-40}$; the factor π^{-1} is included (see Part I, Eqs. (7b)) because in the process of fixation of the methyl radical it ceases to rotate as a separate body and E_1''' contains the entropy due to the two vibrations corresponding to the two rotations. These vibrations are presumably of the carbon-hydrogen bending type, and are approximately[16] 1400 cm^{-1}. We thus get $A_1''=87$, giving $A_1=A_1'A_1''=2.4\times10^{13}\times87=2.1\times10^{15}$. When we double this to allow for the possibility that either methyl can leave, it is still seven-fold too low, as compared to the experimental value. The uncertainties are probably sufficiently great so that this interpretation of the azomethane reaction cannot be excluded on these grounds alone. Nevertheless, other considerations point to it as being rather improbable. Thus, it is obvious from the discussion in §1 that to be consistent with the above picture the activated complex must have the rotations of the methyl group fully excited. In this case there is probably no saddle point in the potential energy when the relative angular momentum of the fragments is zero and so one might have some justification in claiming that the fragments produced in the decomposition actually constitute the activated complex, and in this state the methyl does rotate freely. It does, nevertheless, hardly seem reasonable that the methyl group could be as loosely bound as this at the last point at which it is possible to transfer energy from one degree of freedom to any other of the whole system[23] and,

[19] Ramsperger, J. Am. Chem. Soc. **49**, 912, 1495 (1927).
[20] Ramsperger, J. Am. Chem. Soc. **50**, 714 (1928).
[21] Kassel, *Kinetics of Homogeneous Gas Reactions* (The Chemical Catalog Co., 1932) pp. 192, 196.
[22] Kohlrausch, reference 11b.

[23] See the discussion, last part of §1.

in any event, this surely seems not to be the case with the isopropyl compound.

However (though we still have to account for the difference between azomethane and azoisopropane), if we should be willing to admit that the reverse of the decomposition of azomethane is trimolecular, the large value of A_1 would seem less surprising since the effect would then be divided between two methyl radicals. There is, as a matter of fact, other evidence, which has been discussed by Ramsperger,[24] in favor of the supposition that the reverse reactions of the decompositions of the azo-compounds are trimolecular. The rate of decomposition of methylazoisopropane[24] is given by the expression[25] 2.80×10^{15} exp $(-47{,}480/RT)$ sec.$^{-1}$ and it will be noted that both the energy of activation and A_1 have intermediate values with respect to the other azo-compounds. This suggests that there are certain energies of activation and certain contributions to A_1, which are characteristic of the splitting off of methyl and isopropyl groups, respectively, and that these are independent of the compound.

If this supposition is true, then the activation energy necessary for removal of a methyl radical is greater than that necessary to remove an isopropyl. One is inclined to believe that this excess of energy is connected in some way with the large value of A_1 for azomethane and, indeed, on closer consideration, it seems very likely that this is the case. This can be understood better by a discussion of the reverse reaction. Since the moment of inertia of a methyl radical is small, the hydrogens will be rotating around rather rapidly, and if the methyls approach the nitrogen with just average energy, the hydrogens will get in the way, and except in very rare instances may be expected to prevent the carbon atoms from forming bonds. The reason for this is that the repulsive forces acting between the hydrogens and the nitrogen, will transmit enough momentum to the methyl radical to cause it to reverse its direction. However, if the methyl radical is going fast enough, this is less likely to happen. The force between the hydrogens and the nitrogen will ultimately be dissipated in causing vibrations of the hydrogens or, still more likely, since they have lower frequencies, to the bending vibrations of the molecule, and the hydrogens will simply be dragged in, so to speak, with the relatively heavy carbon atom. It does thus appear likely that some additional energy will be required for the trimolecular association reaction to take place if the recombining groups have small moments of inertia, the large A_1 value being accounted for because it does not much matter what the rotational state of the methyl radical is, so long as it has sufficient translational energy. In the case of the reverse unimolecular reaction we must assume that it is correspondingly difficult for the methyls to leave, unless they have some additional energy, or have the possibility of getting the requisite energy from other degrees of freedom.

Since the moments of inertia of the isopropyl radical are all large, it will be seen that no effect, such as we have assumed to be operative in the case of the methyl radical, is to be expected. The rotation will be relatively slower and it will be difficult for the carbon atom which forms the bond to drag along equally heavy atoms if the orientation is not correct. The difference between methyl and isopropyl radicals is thus to be expected and it is seen that methylazoisopropane, which has one methyl and one isopropyl radical, should be intermediate in all respects to the other two azo-compounds, as is observed.

In the case of azoethane, which D. V. Sickman and O. K. Rice are now attempting to prepare, we have to consider the recombination of ethyl radicals. An ethyl radical has four degrees of freedom of rotation (including one internal free rotation), two of them having large moments of inertia due to rotation of carbon atoms, and the two have small moments of inertia due to rotation of hydrogen atoms. On recombination it will be seen that one of each kind of rotation will be frozen out so that we may well expect that the kinetics of azoethane will be intermediate between azomethane and azoisopropane. A consideration of the rotations which must be frozen out in the case of azo-*n*-propane, indicates that it will behave more like azoethane than azoisopropane. The fact there are no rotations possible which involve hydrogen and at the same time affect the carbon atom which is actually combining or breaking a bond may be a general cause of the abnormal activity of isopropyl radicals in organic reactions

[24] Ramsperger, J. Am. Chem. Soc. **51**, 2134 (1929). See especially p. 2141.
[25] Reference 21, p. 199.

which involve removal of the radical, since it apparently gives a lower energy of activation, which is not completely counterbalanced by the lower value of A_1.

As hexadeuterozaomethane will no doubt be prepared in the next dozen years we may make a remark regarding what it may do according to the theory outlined, for there is the possibility, though not the certainty, of a very striking result being obtained. It may, namely, be the case that the rotation of the trideuteromethyl radical will be sufficiently slow so that the anomalies of the methyl radical will not be evident; if this is true, then hexadeuterozaomethane will resemble the azoisopropane in its kinetics rather than azomethane. In any event, experiments with hexadeuteroazomethane will certainly be of great interest.

9. Conclusion

There are a number of other unimolecular reactions and for some of them the constant A_1 has anomalously low values. This may be because the decomposition involves an electronic transition; in any event it is likely that the mechanism must differ in a fundamental way from that discussed in this paper.[26] The A_1 values for methyl azide and ethyl azide,[27] 3.02×10^{15} and 2.00×10^{14}, are perhaps a little high, but the reaction products are so complex as to make it difficult to speculate as to the initial process and there may, indeed, be short chains involved. The relative A_1 values and the relative activation energies (43,500 and 39,740, respectively) suggest that possibly something similar to what we have postulated for the azo-compounds is involved. The A_1 value for the decomposition of paracetaldehyde[28] 1.3×10^{15} may be rather high but this reaction has rather peculiar characteristics[28b] and may be of a complex nature. The values for parabutyraldehydes[29] are also a little high. We should also remark that the reverse reactions to the bimolecular associations considered in Part I must have rather large A_1 values in view of the small number of rotations apparently frozen out when the associations occur.

Other reactions might be discussed, but our aim has not been to exhaust the possibilities but to give a sufficient discussion to show that there are a considerable number of unimolecular reactions which may be explained on the basis of the hypothesis of "exact orientation" and to illustrate the value of the point of view which has been developed in previous articles. It will be evident that no philosopher's stone has been discovered which will explain all reactions but we believe that we now have at hand a valuable means for classifying reactions and guiding our speculations about them.

We wish to acknowledge our indebtedness to Professor Henry Eyring for helpful discussions with one of us (H. G.).

[26] It may be of interest in this connection to note that in many of these cases, for example, the decompositions of nitryl chloride (Schumacher and Sprenger, Zeits. f. physik. Chemie **B12**, 115 (1931)) and dimethyltriazene (Ramsperger and Leermakers, J. Am. Chem. Soc. **53**, 2061 (1931)) and the isomerization of dimethyl maleate (Nelles and Kistiakowsky, J. Am. Chem. Soc. **54**, 2208 (1932)), the effective number of degrees of freedom calculated on the basis of the Rice-Ramsperger-Kassel theory is smaller than expected from the structure of the molecule.

[27] Leermakers, J. Am. Chem. Soc. **55**, 2719, 3098 (1933).

[28] (a) Coffin, Can. J. Research **7**, 75 (1932); (b) Coffin and Geddes, ibid. **11**, 180 (1934).

[29] Coffin, Can. J. Research **9**, 603 (1933).

The Activation Energy of Unimolecular Reactions. II

O. K. RICE AND HAROLD GERSHINOWITZ,[1] *Chemical Laboratories, Harvard and Princeton Universities*

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The modifications in our earlier paper by the above title, necessitated by recent work on the absolute rate of chemical reactions, are considered, and it is shown that the assumption that the fragments resulting from a unimolecular decomposition must be "exactly oriented" (in the sense of the preceding article) in order to be able to recombine is equivalent to the assumptions made by Kassel in his quantum theory of unimolecular reactions. The relation between the observed activation energy and the energy necessary to break the bond is discussed.

SOME revisions in our first article with the above title[2] are indicated by the results of the preceding paper on the absolute rates of chemical reactions. The conclusions in the former were based largely on the assumption that the reverse of a unimolecular reaction takes place without any energy of activation, provided this reverse reaction involves the recombination of free radicals. Now this assumption is essentially equivalent to the assumption that all energy states of the recombining radicals are equally available for reaction, and this is not consistent with the hypothesis of exact orientation, discussed in the preceding article, but is rather a hypothesis of no orientation. We are now, however, in a better position to find the relation between the energy of activation of a reaction and the energy necessary to break the bond. It is the purpose of this paper to discuss how this may be done and to consider again the nature and validity of the various quantum theories of unimolecular reaction.

It is usual to write the rate of a unimolecular reaction in the form

$$K = Ae^{-\epsilon_a/kT}, \tag{1}$$

where ϵ_a is the energy of activation per molecule, k is Boltzmann's constant, T the absolute temperature and A is a "constant." The usual method of obtaining ϵ_a is to plot $\ln K$ against $1/T$ and draw the best straight line through the experimental points. Since Tolman[3] has shown that $kd \ln K/d(1/T)$ is equal to the difference between the average energy of those molecules which react and the average energy of all the molecules, it is obvious that the experimental value of ϵ_a is equal to this difference of average energies, say for a temperature in the middle of the experimental range; theoretically we define it this way for all temperatures. But now from (1)

$$d \ln K/d(1/T) = d \ln A/d(1/T) - \epsilon_a/k - (1/kT)d\epsilon_a/d(1/T). \tag{2}$$

Since, by Tolman's relationship,

$$d \ln K/d(1/T) = -\epsilon_a/k, \tag{3}$$

we see that

$$kd \ln A/dT = (1/T)d\epsilon_a/dT, \tag{4}$$

the relation between ϵ_a and $k \ln A$ being thus just exactly like that between the average energy and the entropy of an ordinary thermodynamic system. This relationship has indeed been stated in work of La Mer.[4] It must be noted, however, that A is not dimensionless, as would be expected if $\ln A$ were a true entropy term but it has the dimensions of reciprocal seconds.

In the case of a unimolecular reaction in which the reverse reaction requires exact orientation $A = ekT/hE_1'$, where E_1' is the antilogarithm of the entropy factor for the oscillation along the direction of the bond which breaks on reaction. The factor e which is introduced to take care of the effect of the bond which breaks is derived on the assumption that the temperature is high and at low temperatures should be replaced by a quantity, say e', which is dependent on the temperature. We thus get, integrating Eq. (4)

[1] Parker Traveling Fellow of Harvard University.

[2] Gershinowitz and O. K. Rice, J. Chem. Phys. **2**, 273 (1934).

[3] Tolman, *Statistical Mechanics* (Chemical Catalog Co., 1927), pp. 261–2. See also footnote 11 of Ref. 2.

[4] La Mer, J. Chem. Phys. **1**, 289 (1933).

$$\epsilon_a=\epsilon_{a,0}-k\int_0^T T(d\ln E_1'/dT)dT$$
$$+k\int_0^T T(d\ln(e'kT/h)/dT)dT, \quad (5)$$

where $\epsilon_{a,0}$ is the activation energy at °K. Now $k\int_0^T T(d\ln E_1'/dT)/dT$ is simply the average energy above the zero point of the oscillator involved in E_1', while the last term of (5) is seen, from its origin, to be the average energy of a stream of particles flowing out over a potential energy hill, above the minimum energy necessary to get over the hill.[5] For high temperatures, and for all practical purposes for all temperatures this may be set equal to kT. This is, in fact, the value obtained by direct integration, setting e' constant, which would naturally be assumed to give the correct value, as the variation in e' must take place at a very low temperature. Thus the average energy of all the molecules which decompose minus the minimum energy $\epsilon_{a,0}$ necessary for decomposition at °K, which is $\epsilon_a-\epsilon_{a,0}+\bar{\epsilon}$, is equal to the average energy of all the degrees of freedom of the molecule which decomposes except that degree of freedom connected with the bond which breaks, plus kT. Now this is exactly the case in Kassel's quantum theory of unimolecular reactions.[6] But the calculation of the rate constant as a function of pressure in Kassel's quantum theory, as well as in the original Rice-Ramsperger-Kassel theory of unimolecular reactions, depends not alone on the average energy of the molecules which react but on the energy *distribution*. However, by a theorem due to Ehrenfest,[7] if an average energy is known as a function of temperatures for all temperatures the corresponding energy distribution is exactly determined. Hence we may say that Kassel's quantum theory is entirely equivalent to the assumption that exact orientation is required for the reverse reaction at all temperatures. This is, indeed, a fairly obvious result.

Since the distribution of energy of the reacting molecules must be the same for any reaction and its reverse, it is seen that on recombination those degrees of freedom of the fragments which have to be frozen out on association will correspond, as far as their energy distribution (of energy above the zero point energy) is concerned, with the vibrational degrees of freedom which they form. It is natural to suppose that some energy of activation will be required in order to supply the zero point energy, but this cannot be proved definitely, for some of this zero point energy may be furnished by redistribution of energy from the bond which is formed.[8] If this happens the energy of activation of the unimolecular reaction will be correspondingly lowered and at absolute zero the energy of activation will be less than it would be were there no zero point energy. (This energy of activation without zero point energy at 0°K we shall call $\mathfrak{E}_a$ for the unimolecular reaction and the corresponding quantity for the association reaction we shall call $\mathfrak{E}_a'$. The energy of breaking of the bond, $\mathfrak{E}$, is then equal to $\mathfrak{E}_a-\mathfrak{E}_a'$.) On the other hand, if the association does require an energy of activation to provide the excess zero point energy, then the energy of activation at absolute zero would be practically unchanged (changed only by the amount of the zero point energy of the one bond which breaks) if the zero point energy could be wiped out, and we could write, approximately,

$$\mathfrak{E}_a=\epsilon_{a,0}. \quad (6)$$

More generally, if we let $\epsilon'_{a,0}$ be the energy of activation of the association reaction at absolute zero and ΔE_0 the energy of dissociation at absolute zero, we have, as in our former paper,

$$\epsilon_{a,0}=\epsilon'_{a,0}+\Delta E_0 \quad (7)$$

and the relation between ΔE_0, $\mathfrak{E}$, and the change in zero point energy on dissociation, $\Delta\epsilon^0$, namely,

$$\Delta E_0=\mathfrak{E}+\Delta\epsilon^0, \quad (8)$$

gives us finally

$$\mathfrak{E}=\epsilon_{a,0}-\epsilon'_{a,0}-\Delta\epsilon^0. \quad (9)$$

The case in which $\epsilon'_{a,0}=\mathfrak{E}_a'$, and accordingly

$$\mathfrak{E}_a=\epsilon_{a,0}-\Delta\epsilon^0 \quad (10)$$

represents either the case of no orientation, or the case discussed above, in which the extra

[5] See O. K. Rice and Gershinowitz, J. Chem. Phys. **2**, 857 (1934).
[6] Kassel, J. Phys. Chem. **32**, 1065 (1928).
[7] Ehrenfest, Ann. d. Physik **36**, 111 (1911).

[8] Essentially this assumes the rate is not determined by the entropy of a "normal" (see preceding article, §1) activation complex, for at the top of the saddle point no energy is available from the bond to be formed.

zero point is supplied from the energy of the bond formed. The case of no orientation we have discussed in detail in our former paper.[2] In general, unless the process of activation involves some special mechanism such as we assumed in the preceding paper in the case of the decomposition of azomethane, we may assume that $\mathfrak{E}_a$ lies between the values given by (6) and (10), and all present indications are that these will be rather close together, since $\Delta\epsilon_0$ will be of the order of the zero point energy of only a few vibrations (those changed to translations or rotations in the decomposition) most of which are of the bending type. In the case of exact orientation $\epsilon_{a,0}$ may be evaluated from the observed ϵ_a by Eq. (5). The first integral on the right of (5) is less than kT, the other is equal to kT. In this case, therefore, $\epsilon_{a,0}$ may be taken for all practical purposes to be equal to ϵ_a, and $\epsilon_{a,0}$ is a fair measure of $\mathfrak{E}_a$ which is really the fundamental quantity.

If the process of activation does involve a special mechanism such as assumed in the preceding paper for the decomposition of azomethane, then no direct relation exists between the energy of activation and the energy necessary to break the bond.

If we consider the reaction from the point of view of an activation complex, we may say that Kassel's quantum theory of unimolecular reaction is equivalent to the assumption that the frequencies of the activation complex are the same as those of the molecule which is decomposing; the quantum theory of Rice,[9] on the other hand, corresponds to a general lowering of frequencies in the activation complex. The evidence now at hand favors Kassel's hypothesis as the basis of an approximate method for calculating the rate of a unimolecular reaction as a function of pressure.

[9] O. K. Rice, Proc. Nat. Acad. Sci. **14**, 114 (1928).

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The Absolute Rate of Reactions in Condensed Phases

W. F. K. WYNNE-JONES AND HENRY EYRING, *Frick Chemical Laboratory, Princeton University*

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The theory of absolute reaction rates is developed for condensed phases. The equation for the rate of a reaction of any order in any phase where the slow process is the passage over an energy barrier consists of the product of a transmission coefficient κ, a frequency kT/h, an equilibrium constant between an activated complex and the reactants and an activity coefficient factor. Previous theories of reaction rates such as Brönsted's, the collision theory of Mc C. Lewis, etc., are seen to be special cases of the general theory. A variety of examples are considered.

IN a previous paper one of us[1] outlined the theory of the absolute rate of reactions in terms of the activated complex and the probability of its formation from the reacting substances. Here we propose to consider in greater detail the properties of the activated complex and, by application of the equation already derived, to show how the rates of reaction in solution and at interfaces may be calculated. The relation of this treatment to certain empirical generalizations will be considered and the existence of numerous anomalous reaction rates will be explained.

Reaction rates in solution have usually been considered as too complex to yield to any simple treatment and the work of Christiansen[2] and of Norrish and Smith[3] seemed to show that rates in solution were abnormally slow. Moelwyn-Hughes[4] from an examination of a large mass of data showed that for many reactions the rate was not far from that calculated on the simple kinetic

[1] Eyring, J. Chem. Phys. **3**, 107 (1935).

[2] Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).

[3] Norrish and Smith, J. Chem. Soc., 129 (1928).

[4] Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford Univ. Press.

theory using a collision diameter of the same magnitude as for gaseous reactions. However, this attempt to explain reaction rates yields in general only the same qualified success that the method would give if applied to a calculation of equilibrium constants and, since we know that, for the latter, the method is quite crude, we must clearly seek for a more exact treatment of reaction rates.

In the reaction

$$n_1A_1+\cdots+n_iA_i\rightarrow C\rightarrow m_1B_1+\cdots+m_iB_i \quad (1)$$

nA and mB represent n moles of the reacting species A and m moles of the species B, respectively, while C represents the activated complex. The activated complex, C, differs markedly from an ordinary molecule only in that degree of freedom in which it is flying to pieces, that is to say, it has 4 instead of the usual 3 translational degrees of freedom. We can therefore write for the equilibrium between the reacting molecules and the activated complex

$$K=K^{\ddagger}\frac{(2\pi m^{\ddagger}kT)^{\frac{1}{2}}}{h}=\frac{a^{\ddagger}}{a_1^{n_1}\cdots a_i^{n_i}}\frac{(2\pi m^{\ddagger}kT)^{\frac{1}{2}}}{h} \quad (2)$$

where $a^{\ddagger}$ is the activity of the activated complex and a_1 to a_i the activities of the species A_1 to A_i. Later we consider the definitions of the standard state and introduce activity coefficients but first we shall consider states for which the activity may be identified with the concentration

$$K^{\ddagger}=c^{\ddagger}/(c_1^{n_1}\cdots c^{n_i}).$$

We now consider more closely the significance of K and $K^{\ddagger}$. The fact that the activated complex has a fourth translational degree of freedom does not affect the uniqueness of the expression we must write for the specific reaction rate but it does introduce an interesting arbitrariness into the expression for the concentration of the activated complex not present for molecules with but three degrees of freedom. Thus in (2) we have introduced K and $K^{\ddagger}$ both of which might be interpreted as equilibrium constants. For unit concentration of reactants K gives the concentration of activated complexes which would lie within a length of a cm along the fourth internal translation if for the whole cm the density in phase space were just that at the point of passage across the barrier. On the other hand $K^{\ddagger}$ is the equivalent expression for the concentration of activated complexes lying in a single unit, h, of the phase space along this internal translation instead of in the $(2\pi m^{\ddagger}kT)^{\frac{1}{2}}/h$ units for K. In (2) and throughout the paper we have chosen to define $K^{\ddagger}$ as our equilibrium constant. The advantage is that $K^{\ddagger}$has the usual dimensions so that the specific rate of any reaction is simply obtained by multiplying by a transmission coefficient κ and the universal frequency kT/h. The rate equation is then:

$$\begin{aligned}k'&=\kappa\cdot K\cdot\left(\frac{kT}{2\pi m^{\ddagger}}\right)^{\frac{1}{2}}\\&=\kappa\cdot K^{\ddagger}\frac{(2\pi m^{\ddagger}kT)^{\frac{1}{2}}}{h}\cdot\left(\frac{kT}{2\pi m^{\ddagger}}\right)^{\frac{1}{2}}\\&=\kappa\cdot K^{\ddagger}\cdot kT/h. \quad (3)\end{aligned}$$

Further substitution of

$$K^{\ddagger}=e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R}$$

gives

$$k'=\kappa\cdot e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R}kT/h. \quad (4)$$

These equations give the rate of a reaction in any phase provided that the slow process is the surmounting of a potential energy barrier. This is simply an alternative way of expressing Eq. (10) of the previous paper. We here employ the symbol κ instead of c for the transmission factor in order to avoid confusion with concentration.

The equivalence of Eqs. (3) and (4) to (10) of the previous paper is seen when we write the equilibrium constant $K^{\ddagger}$ in terms of the partition functions for the normal molecules and the activated complex

$$K^{\ddagger}=(F_a'/F_n)e^{-E_0/kT},$$

where F_a' is the partition function for all the degrees of freedom of the activated complex except the one along which decomposition is occurring, and F_n the partition function for all the reactants. Since the thermodynamical and statistical mechanical formulations are exactly equivalent, we shall be able, in our subsequent discus-

sion, to use whichever equation happens to be the more convenient for our purpose. This is particularly valuable for reactions in solution as many of the properties of solutions have been experimentally determined and correlated on a thermodynamical basis although their interpretation by statistical mechanics has not often been possible except in rather general terms.

As previously indicated, whenever it is justifiable to regard the reactants simply as hard spheres, this treatment reduces exactly to the usual kinetic theory treatment, but we can show that such conditions will be rare and more or less accidental.

The Transmission Coefficient

The transmission coefficient, κ, represents the probability of the activated complex forming the products after crossing the barrier, i.e., not returning. If the activated complex makes on the average n crossings of the barrier before decomposition then $\kappa=1/n$. From the shape of the potential surface for a given reaction it is possible to estimate the value of κ and frequently this value is very close to unity. The effect of the relative masses of the reacting atoms will be illustrated by consideration of the reaction of an atom with a diatomic molecule.

$$A_2+A_1A_3\rightarrow A_2A_1A_3\rightarrow A_2A_1+A_3.$$

Eyring and Polanyi[5] discussed this reaction in detail and pointed out that for the three atoms colliding along a straight line the mechanics of the reaction can be represented by a mass point moving on a surface made by plotting the potential vertically and using as horizontal axes the two distances between the atoms A_2 to A_1 and A_1 to A_3. These distances must be plotted not at right angles, however, but at an angle of $\theta=90°-\sin^{-1}[(m_2m_3/(m_1+m_2)(m_1+m_3)]^{\frac{1}{2}}$, where the m's are the masses of the three atoms. Thus we see that if either m_2 or m_3 is small compared with the other two masses, the acute angle, θ, approaches 90°. The surface itself consists of two confluent valleys parallel to the two axes. A mass point, representing our system, coming up one valley will, after passing over the intermediate low barrier, either be reflected and return or else pass into the second valley. In the latter case we have reaction. Which of these cases will arise depends on θ and therefore upon the relative masses. How much the two valleys round off into each other at their junction will also have its effect on κ and, as this rounding off will be the greater the more the coulombic or additive binding exceeds the exchange binding, κ should more nearly approach unity as the reactants become more metallic (since the coulombic energy then becomes notably great). Just how near κ approaches unity is thus seen to depend on the ratio of the colliding masses and the nature of the binding forces. Our present knowledge comes from consideration of the approximate surfaces available for some of the simpler reactions for which we can say that κ is of the order unity.

On the other hand a type of reaction for which κ is often small is the adsorption of molecules on solid surfaces. Here the transmission coefficient is to be identified with the accommodation coefficient for that fraction of the molecules which strikes the surface with more than the necessary activation energy for adsorption.

Nature of Equilibrium in the Activated State

There is an important point regarding the activated complex which perhaps more than any other has been generally misunderstood. *It is not necessary that a large fraction of the activated complexes must fail to react in order that the equilibrium concentration be maintained. The activated state is not in general a state of indecision in which the activated complex is uncertain which way to proceed.* When κ is nearly unity an activated complex formed from the reactants will almost certainly decompose into products and whether it will do this or not is entirely independent of how fast the reaction is proceeding in the reverse direction. To say that activated complexes formed from reactants and from products collide and thus help to maintain equilibrium is without meaning as they are moving in spaces corresponding to different coordinates much as two trains passing on parallel tracks. By definition, for a gas reaction all molecules which are together at the activated state are included in the activated com-

[5] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

plex so that the direction in which the activated complex proceeds is a mechanically determined question and is not influenced by the number of activated complexes moving in the reverse direction. For solutions, the direction of decomposition is equally determined by mechanics if we include the solvent molecules in our activated complex. This is also true when we treat the effect of the solvent molecules as an external potential and integrate over the external coordinates of the reacting molecules to obtain $K^{\ddagger}$ in the way usual for equilibrium constants. The solvent molecules simply modify our potential surface but leave unchanged the concept of a mass point passing over a barrier. Now, since we can use equilibrium statistics when there are an equal number of activated complexes proceeding in both directions, we can still use it if those in one direction are completely suppressed, provided, of course, there is no autocatalysis. Thus if $\kappa=1$ and we start out with reactants but no products the number of activated complexes going in the forward direction is exactly the equilibrium number and there are none going in the reverse direction. If some activated complexes collide with the surface and then return, the number moving in the forward direction will be fewer than the equilibrium number by the factor κ. If there is autocatalysis there are then two separate mechanisms which are important; one in which the activated complex contains the reaction products and one in which it does not. The previous considerations apply then to each separate mechanism whether there be one or a dozen. Chain reactions are simply built up of a series of successive reactions each of which is to be treated as we have indicated. This aspect of the theory of the activated complex is given particular prominence, as it is in sharp contrast with the commonly held view in which it is assumed that, only when most of the activated complexes fail to react (i.e., $\kappa \ll 1$), can one assume that the equilibrium numbers are moving in a given direction. The nature of the activated complex thus becomes clearly apparent when considered in terms of a potential surface.

Reaction in a Condensed Phase

As we have seen, we can write for the specific reaction rate constant

$$k'=\kappa\cdot K^{\ddagger}kT/h\cdots \tag{3}$$

or,
$$k'=\kappa\cdot(F_a/F_n)e^{-E_0/RT}kT/h\cdots, \tag{5}$$

providing our standard state has been defined so that the activities a_i can be identified with the concentration c_i. In the present unsatisfactory condition of the theory of condensed phases there is a real advantage in choosing the dilute gas as the standard state. Then for any condensed state we must write:

$$K^{\ddagger}=a^{\ddagger}/(a_1\cdots a_n)=\alpha^{\ddagger}c^{\ddagger}/(\alpha_1\cdots\alpha_n\cdots c_1\cdots c_n)$$

and for the rate $(c_1\cdots c_nk')$

$$=\kappa\cdot c^{\ddagger}\cdot kT/h,$$

giving the specific rate

$$k'=\kappa\cdot K_0^{\ddagger}\cdot(\alpha_1\cdots\alpha_n/\alpha^{\ddagger})\cdot kT/h\cdots, \tag{6}$$

where the a's are the activities and the activity coefficients α_i and $\alpha^{\ddagger}$ approach unity as the gas becomes infinitely dilute. When the reaction proceeds in a phase other than the gaseous we still retain the gaseous state as the standard and as long as the gas phase is sufficiently near the ideal the α's have the significance of distribution coefficients between the two phases.

Our choice of the infinitely dilute gas as the standard state irrespective of the phase in which the reaction is proceeding has the great advantage that in the statistical mechanical calculation for the standard state we can restrict our attention to the reacting particles. If it is desirable to use statistical mechanics to calculate the activity coefficients, two avenues are open: we may treat the adjacent molecules either as entering into a larger activated complex, or as constituting a field in which the reacting molecules move. Either treatment simply has the effect of increasing the number of degrees of freedom for which the potential energy must be considered and leaves unchanged the general problem of the passage of an activated complex across a potential barrier.

For a reaction proceeding in solution we see that the rate is greater than in the dilute gas by the factor $(\alpha_1\cdots\alpha_n)/\alpha^{\ddagger}$ and it is clear that exact cancelation of the activity coefficients will be fortuitous and that, in general, a reaction is likely to proceed at a different rate in solution

than in the gaseous state. For the exact calculation of the rate, a knowledge of distribution coefficients is essential and we will indicate briefly the method of introducing into our equation certain empirical generalizations.

For the distribution of a substance between its pure liquid phase and the gaseous phase several rules have been advanced of which the most valuable are Trouton's rule, its modification by Hildebrand and a more recent formulation by Langmuir.[6] Using Langmuir's Eq. (29) for the vapor pressure in atmospheres one readily obtains the equation $p=2.5e^{\frac{1}{2}}T^{\frac{1}{2}}e^{-\Delta H/RT}$, which together with an average value of 0.027 for the concentration in moles per cc in the liquid phase, gives as a general equation for the distribution ratio between the liquid and gaseous states for nonassociated liquids

$$\alpha=5.0T^{\frac{1}{2}}e^{-\Delta H/RT}. \tag{7}$$

Over a temperature range extending from a few degrees absolute to some thousands of degrees, although α is of the order 10^3, this equation represents the data within 2 or 3-fold for such diverse substances as fused salts, the halogen acids and the elements both metallic and nonmetallic. If, instead of the value 0.027, the actual liquid concentration is employed, Langmuir's calculations show that the discrepancy is usually not more than 40 percent. For certain associated liquids, however, such as water and ammonia, the numerical constant in the above equation is about 30 instead of 5.[7]

While these considerations apply to pure liquids we may readily extend them to solutions. If the solutions are ideal then clearly Eq. (7) applies; even if the solutions are nonideal, if the deviation arises principally from variation in the heat of vaporization then the equation is still applicable.

Frequently instead of using the approximate equation we may employ more accurate experimental data such as are available in the form of solubility coefficients of gases and vapor pressures.

[6] Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).

[7] This equation applies only up to pressures of a few atmospheres. At the critical point α is of course unity. A more exact equation would take account of the decrease in the temperature dependence of α by including terms in the denominator of the general form $\{1-\exp(-h\nu/kT)\}^{-1}$.

Unimolecular Reactions

For any unimolecular reaction in the liquid phase we may write Eq. (6) in the form

$$k'=\kappa\cdot K_0^{\ddagger}\alpha_1/\alpha^{\ddagger}\cdot kT/h \tag{8}$$

and we can distinguish three cases: (1) If the activated complex and the normal molecules both form ideal solutions in a solvent then, since by definition there is no heat of mixing, we see from Eq. (7) that $\alpha/\alpha^{\ddagger}=1$ hence

$$k'=\kappa\cdot K_0^{\ddagger}\cdot kT/h,$$

that is to say, the reaction will proceed at the same rate as in the gaseous state. (2) If the deviations from ideality are due mainly to changes in the heat of vaporization (ΔH) then the α's may not cancel but their ratio will introduce a factor giving the equation

$$k'=\kappa\cdot K_0^{\ddagger}\cdot e^{-(\Delta H-\Delta H^{\ddagger})/RT}\cdot kT/h$$

and the exponential term simply leads to a change in the apparent activation energy. (3) If the numerical factor is affected and to a different extent for the reacting molecules and the activated complex, as would happen if solvation of the various species occurred, we have the case where not only the apparent activation energy but also the factor multiplying it may be considerably altered.

If we know the reaction rates in solution and in the gas phase together with the partial pressures of the reactants we can deduce the partial pressure of the activated complex: this is true for reactions of any order. With the knowledge of the vapor pressure of the activated complex thus obtained we can go very far in excluding certain types of mechanism. Thus, if the data lead to a value of the vapor pressure of the activated complex which is compatible with Eq. (7) using a value of ΔH which is at least approximately in agreement with Langmuir's[8] ideas of molecular surface energy, it is highly probable that the activated complex in solution is unchanged and homopolar. A change in mechanism as between the two phases will in general lead to an abnormal value for the apparent vapor pressure of the activated complex.

[8] Langmuir, Chem. Rev. **6**, 451 (1929).

The classical example of a unimolecular reaction which has been studied in several phases by Daniels and his collaborators[9, 10] is the decomposition of N_2O_5 which in a variety of "inert" solvents proceeds with the same specific reaction rate as for the gas. By reference to the last column of Table V of the paper by Eyring and Daniels we see that $\alpha/\alpha^{\ddagger}$ for saturated solutions of N_2O_5 in nitromethane, carbon tetrachloride and liquid N_2O_4 are 1.71, 2.32 and 2.01, respectively, whereas the next to the last column shows us that the corresponding values of α for nitromethane and carbon tetrachloride are 740 and 1108, respectively. These values of α are about what one would expect for an ideal solution. The values for the ratio $\alpha/\alpha^{\ddagger}$ indicate that the activated complex likewise has the vapor pressure of a practically normal molecule. N_2O_5 does not decompose in the interior of a crystal in spite of the fact that the activity of the normal molecule is the same as that in the gas so that the activity coefficient is approximately the same as in concentrated N_2O_5 solutions. The reason is that the activity coefficient of the activated complex is enormously high, since, for a molecule in a lattice to form the activated complex, it must displace a great number of molecules thus placing the complex itself under tremendous pressure and leading to a correspondingly high value for the activity coefficient, $\alpha^{\ddagger}$.

Our reaction rate Eq. (3) in the form

$$k' = \kappa \cdot K \cdot (kT/2\pi m)^{\frac{1}{2}}$$

applies equally well for the process of sublimation, vaporization or desorption. When the activation energy is equal to the latent heat then K is the ratio of equilibrium concentrations of gas, c, to condensed molecules, c_s. The actual rate will then be given by

$$k' c_s = \kappa \cdot (K \cdot c_s)(kT/2\pi m)^{\frac{1}{2}}, \qquad (9)$$

where the quantity $(K \cdot c_s) = c_1$ is simply the value deduced from vapor pressure measurements. The rate equation owes its simple form in this case to the fact that the activated complex is to be identified with the vapor molecules.

N_2O_5 decomposes at 45°C in nitric acid at 0.042 times and in propylene chloride at 0.155 times the rate in the gas; hence, we deduce that, for these solvents, either the vapor pressure of the normal molecules is low or the vapor pressure of the activated complex is high by comparison with the normal solvents. Eyring and Daniels' suggestion that the slow rate was due to the formation of a stable complex assumes, of course, that the low value of $\alpha/\alpha^{\ddagger}$ is due to α being low. Vapor pressure or solubility measurements will resolve this question. In general we should expect that abnormal solubility, which of course makes α low, will arise from abnormal solvation thus encasing the molecule in a sheath which may make $\alpha^{\ddagger}$ high for the same sort of reasons as for a molecule in the interior of a crystal. Whether $\alpha^{\ddagger}$ is increased or decreased depends on whether the solvent adds to the reactant in such a way as to strengthen or weaken the bond to be broken. There is a further point to be discussed in connection with this reaction. Since we know the actual rate of the reaction and also the heat of activation our theoretical equation enables us to evaluate the entropy of activation. The experimental results for the decomposition of N_2O_5 in the gas phase are represented by the equation

$$k' = 5.08 \times 10^{13} e^{-24{,}700/RT}.$$

We take the transmission coefficient as unity, since it can hardly differ materially from this value for this reaction, and, by equating the above experimental result to the theoretical value for k', we find that the activated complex is 4.27 units richer in entropy than the normal molecules. This is a typical result for many unimolecular reactions.[11]

We will now use our general theory to calculate the steric factor for one of the elementary processes of a chain reaction postulated by F. O. Rice.[12] The reaction is the formation of a five-membered ring and a methyl radical from the normal hexyl radical: the activated complex will be an almost closed five-membered ring with the methyl radical in the act of leaving the ring. From the data of Parks and Huffman[13] we find that the

[9] Lueck, J. Am. Chem. Soc. **44**, 757 (1922).
[10] Eyring and Daniels, J. Am. Chem. Soc. **52**, 1473, 1486 (1930).
[11] Polanyi and Wigner, Zeits. f. physik. Chemie Haber Band, 439 (1928).
[12] F. O. Rice and K. K. Rice, *Aliphatic Free Radicals* (1935).
[13] Parks and Huffman, *Free Energies of Some Organic Compounds* (1932).

entropy of cyclopentane is about 21 units less than that for normal pentane at 25°C; the formation of the ring changes 4 rotations into vibrations so that the difference in entropy should increase with temperature approximately as $4/2\ R \ln T$. This leads to an entropy change for this ring closure at 650°C of about 25.6 units which corresponds to a steric factor of 2.5×10^{-6} as compared with Rice's estimate of 10^{-6}. This approximate calculation could be improved by taking account of the vibration frequencies in the ring by the formula $\prod_{i=1}^{4} 1/(1-e^{-h\nu_i/kT})$. However, as it stands, it is certainly correct to better than a power of ten. Thus, such a calculation gives a quantitative theory for the change of the steric factor with temperature, something quite impossible on previous ideas about reaction rates.

There is another type of unimolecular reaction occurring in solution which, although requiring an activation energy of as much as 35,000 calories, still proceeds at a measurable rate at room temperatures. In the past this has been interprepreted on the assumption that the slow process is the transfer of energy in collision yielding an activated molecule with the energy, E, distributed among $F+1$ classical degrees of freedom giving the equation

$$k'=Ze^{-E/RT}(E/RT)^F 1/F!,$$

where Z is the number of collisions. This point of view forces Moelwyn-Hughes,[14] in order to explain the rapid reaction rate, to assume that the slow process is the transfer of energy between solvent molecules and the molecule decomposing. That, in solution, this should be the slow process, seems highly improbable when we realize that here if ever we should have the high pressure rate. That it is necessarily the mechanism is certainly untenable, as we see from our conception of an activated complex.

Although the theory invoking a collision and $F+1$ degrees of freedom is on the whole highly arbitrary it does at least take into account more degrees of freedom than are considered in the simple collision theory. Eq. (4) shows that the effect of these other degrees of freedom manifested in the entropy of activation must be considered in chemical reactions.

TABLE I. *Decomposition of Et_3SBr in benzyl alcohol-glycerol mixtures.*

% Benzyl alcohol	ΔS	$\Delta S^{\neq}$
100	20.85	20.42
90.23	17.25	15.86
80.39	13.14	12.91
69.39	6.80	11.07

An example of this type of reaction is the decomposition of triethylsulphonium bromide in various solvents. Taking the data of Corran,[15] which have been used by Soper[16] for demonstrating the analogy between the rate of the reaction and the entropy of the equilibrium process, we have calculated the entropies of activation which are given in column 3 of Table I.

The striking correspondence between the entropy change for the reaction (column 2) and the entropy of activation shows us that the activated complex must resemble closely the products of the reaction. This is in marked contrast to the behavior of the N_2O_5 molecule where the activated complex had an entropy close to that of the decomposing molecule.

BIMOLECULAR REACTIONS

When we come to bimolecular reactions in solution we find that there are reactions which according to the collision theory proceed too fast, too slow and at a normal rate.

Of the first type we have the reverse reaction to that considered above, the association of diethyl sulphide and ethyl bromide to form triethylsulphonium bromide. This reaction proceeds at a reasonable rate at 80°C in pure benzyl alcohol although it has the rather high activation energy of 28,400 calories as deduced from Corran's equilibrium measurements. A kinetic theory calculation yields for the collision diameter the value 1.14×10^{-7} cm instead of the normal value of 2 or 3 Angstroms. Such an interpretation throws the entire responsibility on the translational coordinates and so leads to this impossibly large collision diameter. The conception of the activated complex places a part of the responsi-

[14] Moelwyn-Hughes, *Kinetics of Reactions in Solution* (1933), p. 163.

[15] Corran, Trans. Faraday Soc. **23**, 605 (1927).

[16] Soper, Chem. Soc., Discussion 45 (1931).

bility on the internal coordinates and we see at once that, since the unimolecular decomposition has an entropy of activation practically equal to the total entropy change for the equilibrium process, the bimolecular reaction must proceed with zero entropy of activation instead of the 7 units for a bimolecular reaction in solution[17] required to give agreement with kinetic theory.

A further example of an abnormally rapid reaction is the conversion of ammonium cyanate into urea

$$NH_4^+ + CNO^- = (NH_2)_2CO.$$

The energy of activation for this reaction in aqueous solution is 23,170 calories and from equation (4) we have $\Delta S^{\ddagger} = 0.9$.[18]

Moelwyn-Hughes[19] has compiled a list of reactions in solution which proceed at nearly the rate calculated from the collision theory. For reasons of space we will not include here the complete table of entropies of activation which we have computed for these reactions but merely state that where the reaction rate is just equal to that calculated by Moelwyn-Hughes the entropy of activation is 7 units. A departure by a factor of ten in either direction gives a corresponding change of 4.6 units in $\Delta S^{\ddagger}$. These "normal" reactions involve a neutral molecule and an ion as reactants and consequently the activated complex will carry the same charge as the ion and hence we should expect that the entropy due to solvation would not be much changed as between the reactants and the activated complex. It is, therefore, to be expected that such reactions should involve about the same entropy of activation as analogous gas reactions.[19a]

Of the reactions which proceed at an abnormally slow rate, one large class is that involving salt formation as in the Menschutkin reaction

$$(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4NI.$$

A number of these reactions have been tabulated by Moelwyn-Hughes[20] and the values we have calculated for their entropies of activation range from 25 to 50 units. In general, if for a given equilibrium there is a large entropy change, it is inevitable that either the forward or the reverse reaction proceeds at an abnormal rate. Not many equilibrium data are available but from the results of Essex and Gelormini[21] for the reaction

$$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$$

occurring in nitrobenzene at 60°C we calculate the entropy change for the equilibrium is 54.1 units while $-\Delta S^{\ddagger}$ is 37.5. This suggests that the activated complex is strongly polar and has many solvent molecules oriented around it. In a nonpolar solvent instead of orientation of solvent molecules there will be orientation of the reactants and products. This change in behavior on going from a polar to a nonpolar solvent is well exemplified by the data for the reaction between triethylamine and ethyl bromide in mixtures of acetone and benzene. We see from the figures in column 3 that the entropy of activation remains nearly constant so long as there is an appreciable number of acetone molecules which can be oriented around the activated complex but in pure benzene there is a markedly greater decrease in the entropy of the activated complex.

TABLE II. $(C_2H_5)_3N + C_2H_5Br$ *in acetone-benzene mixtures.*

% Acetone	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$
100	11,710	41.29
80	12,100	40.32
50	12,040	41.64
20	12,180	42.42
0	11,190	48.09

The known behavior of electrolytes in different solvents and in particular the investigations of Kraus and his co-workers[22] into the properties of electrolytic solutions in nonpolar solvents is in harmony with these suggestions of solvent orientation and solute association.

Quite recently Williams and Hinshelwood[23]

[17] For a bimolecular reaction at about 50–100°C a kinetic theory collision diameter of 2A is equivalent to an entropy of activation of 6.9 while a diameter of 3A corresponds to 5.3 entropy units.

[18] Walker and Hambly, J. Chem. Soc. **67**, 746 (1895)

[19] Moelwyn-Hughes, *Kinetics of Reactions in Solution* (1933), p. 79.

[19a] Even for a "normal" reaction the rate in solution is greater by the activity factor $\alpha_1\alpha_2/\alpha^*$. Part of this factor is reflected in a smaller absolute value of the entropy of activation.

[20] Moelwyn-Hughes, *Kinetics of Reactions in Solution* (1933), p. 111.

[21] Essex and Gelormini, J. Am. Chem. Soc. **48**, 882 (1926).

[22] Kraus and Hooper, Proc. Nat. Acad. Sci. **19**, 939 (1933); Kraus and Vingee, J. Am. Chem. Soc. **56**, 511 (1934); Kraus, Trans. Electrochem. Soc. **66**, 179 (1934).

[23] Williams and Hinshelwood, J. Chem. Soc., 1079 (1934).

TABLE III. *Benzoylation of amines in benzene.*

Amine	Acid chloride	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$
H	p.NO_2	5,900	40.22
p.CH_3	H	6,800	38.54
H	p.Cl	7,000	39.97
H	H	7,350	39.62
H	p.CH_3	8,000	39.24
p.Cl	H	7,600	41.83
m.NO_2	H	10,500	39.17
p.NO_2	p.NO_2	10,400	42.52
p.NO_2	H	11,800	39.50

have studied the benzoylation of certain amines and in conformity with the previous work of Bradfield[24] have shown that while these reactions proceed at a rate about a million times slower than that predicted by kinetic theory considerations the steric factor that they introduce is nearly the same for each reaction. In Table III we give the values of $-\Delta S^{\ddagger}$ for these reactions.

The reactions all involve substituted anilines reacting with various substituted benzoyl chlorides and we indicate in column 1 the particular substituent in the aniline molecule and in column 2 the substituent in the benzoyl chloride. The reaction in each case is of the type

$$C_6H_5NH_2+C_6H_5COCl=C_6H_5NHCOC_6H_5+HCl$$

and the activated complex will consist of the two reacting molecules linked between the N atom and the carbonyl carbon atom with hydrogen and chlorine ions in the act of splitting off. This activated complex will be strongly polar and the high entropies of activation are in accord with this. It is interesting to note that, whereas the energies of activation vary considerably, the entropy is practically the same for each reaction. This constancy of the entropy of activation is to be expected since the strongly polar portion of the activated complex is the same in each case. On the other hand the variation of the energy of activation receives a simple explanation in terms of the dipole effects of the substituent groupings as has been pointed out by Williams and Hinshelwood who find that the equation of Nathan and Watson[25]

$$E=E_0\pm c(\mu-\alpha\mu^2)$$

is applicable for these reactions.

[24] Bradfield, Jones and Spencer, J. Chem. Soc., 2907 (1931).

[25] Nathan and Watson, J. Chem. Soc., 2436 (1933).

Baker and Nathan[26] have recently published the results of a study of the reaction between various substituted benzyl bromides and pyridine or α-picoline. The values of $-\Delta S^{\ddagger}$ calculated from their data vary from 20 to 40 units depending upon the particular reaction and the solvent. These values are similar to those quoted above for the Menschutkin reaction and support the idea that the activated complex has a strongly polar structure possibly of the type suggested by Baker and Nathan

$$C_5H_5N^+Ar\overline{Br}.$$

One more point should be emphasized in connection with reactions in which the charge on particular atoms changes during the reaction. If the change in charge occurs before or after the system reaches the activated state then our treatment of the slow process as adiabatic is complete. If the change in charge coincides with and is partly responsible for the slow process (i.e., the potential surface for our reacting system is formed from two surfaces corresponding to different atomic charges, intersecting at the activated state) then a part of the chemical inertia which we have included in the term $\Delta S^{\ddagger}$ should be interpreted instead as a slowness of transition from one surface to the other. In the present state of our knowledge of potential surfaces for reaction in solution a more definitive statement can hardly be made. However, when there is a large overall entropy change for the reactions it is very reasonable to assume that the observed slowness arises simply from the low entropy of the activated state. The possibility that a very slow reaction may be nonadiabatic must not be overlooked. If the apparent entropy of the activated state is as high or higher than would be expected for a similar molecule the reaction is probably adiabatic otherwise it is suspect.

ACID AND BASE CATALYSIS

Another group of reactions of great interest is that included under the general description of acid and basic catalysis. These reactions have been intensively studied of recent years especially in the laboratories of Brönsted and Dawson and an excellent review of their main features is given

[26] Baker and Nathan, J. Chem. Soc., 519 (1935).

in an article by Pedersen.[27] Brönsted and Pedersen first proposed the relation

$$k' = GK^x$$

where k' is the specific rate constant for a reaction which treats the catalyst as a reactant and where K is the dissociation constant of any acid or base. G and x are independent of the catalyst for a given reaction at a definite temperature. If x is independent of the temperature we have

$$d \ln k'/dT = x \cdot d \ln K/dT + d \ln G/dT \quad (10)$$

and, as ΔH for the ionization of many weak acids with a dissociation constant of about 10^{-5} at room temperature is approximately zero,

$$d \ln k'/dT \sim d \ln G/dT,$$

that is to say the energy of activation is nearly the same for different catalysts. This is shown by the work of Kilpatrick, Pedersen and Smith.[28, 27] Without introducing this approximation we may write (10) in the form

$$(\Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R) = x \cdot (\Delta H/RT - \Delta S/R) - \ln G \quad (11)$$

and set

$$\Delta H^{\ddagger} = x \cdot \Delta H - \Delta H_G, \quad (11a)$$

$$\Delta S^{\ddagger} = x \cdot \Delta S + \Delta S_G, \quad (11b)$$

where ΔH_G and ΔS_G are the energy and entropy components of $\ln G$. Pedersen has shown that in the bromination of acetoacetic ester the above Eq. (11a) for the energy of activation holds quite well using the same x for the various basic catalysts that he employed.

The results of Smith for the iodination of acetone enables us to calculate the values of $\Delta S^{\ddagger}$ given in Table IV. The first three columns are self-explanatory, the fourth contains the value of the entropies of ionization of the various acids calculated from the data of Harned and Embree.[29] To make the data consistent with the assumed formula for hydrogen ion OH_3^+ the usual dissociation constants of all the other acids are divided by 55.5. In column 5 we give the values obtained by adding half the entropy of ionization to the entropy of activation for the hydrogen-catalyzed reaction. Columns 3 and 5 now show a very interesting agreement. Column 6 contains the figures given by Smith for the steric factor (which on the collision theory must be introduced to account for the observed rates) divided by the square root of the dissociation constant. The figures given for dichloroacetic acid in columns 4 and 5 are those required to fit the experimental entropy of activation given in column 3. In the absence of accurate data for the dissociation constant of this acid this value of ΔS may be regarded as a provisional estimate.

TABLE IV. *Iodination of acetone in aqueous solution.*

Catalyst	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$-\Delta S$	$-(10.4 + \Delta S/2)$	$P/K^{\frac{1}{2}}$
OH_3^+	20,680	10.4	0	10.4	0.021
$Cl_2CH.COOH$	19,230	16.9	(13.0)	(16.9)	0.025
$ClCH_2.COOH$	19,230	21.2	25.1	23.0	0.016
$CH_3.COOH$	20,010	24.2	30.1	25.4	0.033
$C_2H_5.COOH$	19,370	26.7	30.9	26.3	0.011

It is not necessarily true that x has the same value in Eqs. (11a) and (11b) and it may well be that some of the departures from linearity in the plots of $\log k'$ *vs.* $\log K$ are due to this cause.

The Brönsted Equation

We have seen that Eq. (6) gives the rate of a reaction in any phase in terms of that in the gas phase. However, in any given solvent it is convenient to employ activity coefficients which are defined with respect to a standard state in that solvent—the infinitely dilute solution—and consequently we will separate the factor $(\alpha_1 \cdots \alpha_n)/\alpha^{\ddagger}$ into two terms. The first term will represent the distribution coefficient between the standard states for the liquid and gas whereas the second will give the activity coefficient factor in the solvent. We then rewrite Eq. (6) in the form

$$k' = (\kappa \cdot K_0^{\ddagger} \cdot ((\beta_1 \cdots \beta_n)/\beta^{\ddagger})(kT/h)) (f_1 \cdots f_n)/f^{\ddagger}. \quad (12)$$

The factor $(f_1 \cdots f_n)/f^{\ddagger}$ is simply the Brönsted activity factor and the remarkable success in the interpretation of salt effects which has been achieved by application of the Brönsted equation is too well known to require recapitulation here.

[27] Pedersen, *Den Almindelige syre og Basekatalyse*, Copenhagen 1932.

[28] Kilpatrick and Kilpatrick, J. Am. Chem. Soc. **53**, 3898 (1931); Smith, J. Chem. Soc., 1744 (1934).

[29] Harned and Embree, J. Am. Chem. Soc. **56**, 1050 (1934).

The above equation goes beyond that of Brönsted in that it provides a theory for the quantity in parenthesis.

The critical complex of Brönsted's theory has been variously interpreted. Brönsted[30] himself refers to it as being formed by collisions between the reacting molecules and as decomposing instantaneously into the products, while Bjerrum[31] treats it as a molecule with a life which is long compared with the duration of a collision. As we have already stated there is no such ambiguity about the description of the activated complex which is simply a molecule in statistical equilibrium with the reactants and which is actually in the act of flying to pieces having a mean life which we can take as h/kT. The fleeting existence of the activated complex might be regarded as making inapplicable the usual rules for activity coefficients and of course for electrically charged complexes we have the problem that whereas the time of relaxation of the ion atmosphere is of the order 10^{-10} second the life of the activated complex is only 1.6×10^{-13} second at ordinary temperatures. However, this apparent difficulty is not real, since the molecules which come together and form the activated complex will be those which are already within one mean free path and will therefore have reciprocally modified their ionic atmospheres in such a way as to make a combined atmosphere approximating to that of the activated complex. The Brönsted activity factor therefore gives a precise description of the behavior of a reaction with changing medium and the activity coefficients involved are purely thermodynamical quantities. Of course, it is true that localization of charges in the activated complex will make its activity coefficient depend upon the ionic strength in some less simple manner than for symmetrical ions, but this problem is not peculiar to reaction rate studies but occurs equally in ordinary equilibria. La Mer and Kamner[32] have made accurate measurements on the rate of the reaction between β-bromopropionate and thiosulphate ions and have found that, on the mechanism they assumed, the activity factor is of opposite sign to that predicted from the Brönsted equation. They suggest as explanation that the localization of the charge on the bromopropionate ion results in an abnormal activity coefficient for the activated complex. Sturtevant[33] has shown that disymmetry of the field does not affect the validity of the Debye-Hückel limiting equation for activity coefficients and, since we have shown that the same considerations are valid for the activated complex as for ordinary molecules, we conclude that, if the results of La Mer and Kamner are as accurate as they appear, some other mechanism must be sought for this reaction.

The present theory of rates reduces the problems of kinetics to a thermodynamic calculation of an equilibrium constant for the activated complex and the calculation of a transmission coefficient which is frequently very near unity. The principal problems are thus seen to be those always met in calculating an entropy and a heat of reaction. The difficulties in the simple kinetic picture are thus seen to disappear when viewed in the light of the general theory.

One of us (W. F. K. W-J) is indebted to the Leverhulme Trustees for a fellowship and to the University of Reading for leave of absence.

Note added in proof: Of the two definitions for the equilibrium constant used here and in the previous article[1] Evans and Polanyi (Trans. Faraday Soc. **21**, 875 (1935), in a paper which has appeared while this article was in press have employed the one which requires multiplication by the velocity normal to the energy barrier (and of course the transmission coefficient κ) to give the absolute rate. We also have chosen this definition for processes (such as vaporization or adsorption) where the energy barrier is localized between two phases. For processes inside a single phase we use the definition for which the equilibrium constant must be multiplied by the frequency kT/h and the transmission coefficient κ to give the absolute rate. This difference in choice of the equilibrium constant is a formal one which will be ultimately decided on the basis of utility.

Our value of $5T^{\frac{1}{2}}=87$ at room temperature (see Eq. (7)) for the apparent ratio of bimolecular collisions in the liquid to the gaseous state agrees with their factor of about 100.

[30] Brönsted, Zeits. f. physik. Chemie **102**, 109 (1922); **115**, 337 (1925).
[31] Bjerrum, Zeits. f. physik. Chemie **108**, 82 (1924).
[32] La Mer and Kamner, J. Am. Chem. Soc. **53**, 2832 (1931).
[33] Sturtevant, J. Chem. Phys. **3**, 295 (1935).

Perfect Ternary Solid Solutions

HARRY SELTZ, *Department of Chemistry, Carnegie Institute of Technology*
(Received May 18, 1935)

In this paper equations are developed for calculating the solidus and liquidus surfaces, with tie-lines, for ternary systems showing complete solid solubility, based on the assumption that both liquid and solid solutions are perfect. The forms of the liquidus and solidus isotherms predicted by these equations are considered for an hypothetical example. The ternary system of gold, copper and nickel is shown to deviate markedly from ideal behavior at low mol fractions of gold, even though the copper-nickel system is practically ideal in its binary behavior.

IN a recent publication[1] equations were derived for calculating the liquidus and solidus curves for binary systems which solidify with the formation of solid solutions, based on the assumption of perfect solution behavior in both phases. For a system of two components "A" and "B" melting at T_A and T_B respectively the mol fraction of "B," N_B, of the liquidus at a temperature T was given by the equation,

$$N_B=(1-k_Ae^{\Delta H_A/RT})/(k_Be^{\Delta H_B/RT}-k_Ae^{\Delta H_A/RT}) \quad (1)$$

and for the equilibrium solidus at this temperature, the mol fraction N_B' was given by the relation,

$$N_B'=N_Bk_Be^{\Delta H_B/RT}, \quad (2)$$

where ΔH_A and ΔH_B are the heats of fusion of the pure components and $k_A=e^{-\Delta H_A/RT_A}$ and $k_B=e^{-\Delta H_B/RT_B}$. The system copper-nickel was shown to be almost ideal and recently the liquidus curve for the system[2] H_2O-D_2O has been shown to agree with Eq. (1).

In this paper equations are derived for calculating the liquidus and solidus surfaces for a three-component system showing complete solid miscibility, again assuming that Raoult's law is obeyed by the three components over the entire composition range in both liquid and solid solutions.

Derivation of the Equations

Following the treatment used for the binary system,[1] the necessary equations are here derived from a consideration of the fugacities of the components in the two phases. If Raoult's law is obeyed, then at every temperature and composition,

$$f_A=N_Af_A^\circ, \quad f_B=N_Bf_B^\circ, \quad f_C=N_Cf_C^\circ \quad (3)$$

where f_A is the fugacity of component "A" in a solution containing a mol fraction N_A of that component, and where f_A° is the fugacity of pure liquid A at the temperature in question. Similarly, f_B and f_C are the fugacities of the "B" and "C" components. For the solid phase also,

$$f_A'=N_A'f_A^{\circ\prime}, \quad f_B'=N_B'f_B^{\circ\prime}, \quad f_C'=N_C'f_C^{\circ\prime} \quad (4)$$

with the primes denoting the corresponding terms for the solid state. At any temperature between the melting points of the highest and lowest melting components an isothermal section of the ternary diagram will show two curves, one for the liquidus and one for the solidus, with tie-lines connecting the phases in equilibrium. An infinite number of such equilibrium pairs exist, but for a given pair, $f_A=f_A'$, $f_B=f_B'$ and $f_C=f_C'$ and from Eqs. (3) and (4), $N_A'=N_Af_A^\circ/f_A^{\circ\prime}$, $N_B'=N_Bf_B^\circ/f_B^{\circ\prime}$ and $N_C'=N_Cf_C^\circ/f_C^{\circ\prime}$. Furthermore, as shown in the previous paper,[1] neglecting the change in the heats of fusion with change of temperature,

$$f_A^\circ/f_A^{\circ\prime}=k_Ae^{\Delta H_A/RT}, \quad f_B^\circ/f_B^{\circ\prime}=k_Be^{\Delta H_B/RT},$$
$$f_C^\circ/f_C^{\circ\prime}=k_Ce^{\Delta H_C/RT}$$

whence

$$N_A'=N_Ak_Ae^{\Delta H_A/RT}, \quad N_B'=N_Bk_Be^{\Delta H_B/RT},$$
$$N_C'=N_Ck_Ce^{\Delta H_C/RT}. \quad (5)$$

These equations must be satisfied simultaneously for a condition of equilibrium. At the same time,

$$N_A+N_B+N_C=1, \quad N_A'+N_B'+N_C'=1. \quad (6)$$

[1] Seltz, J. Am. Chem. Soc. **56**, 307 (1934).
[2] La Mer and Baker, J. Am. Chem. Soc. **56**, 2641 (1934).

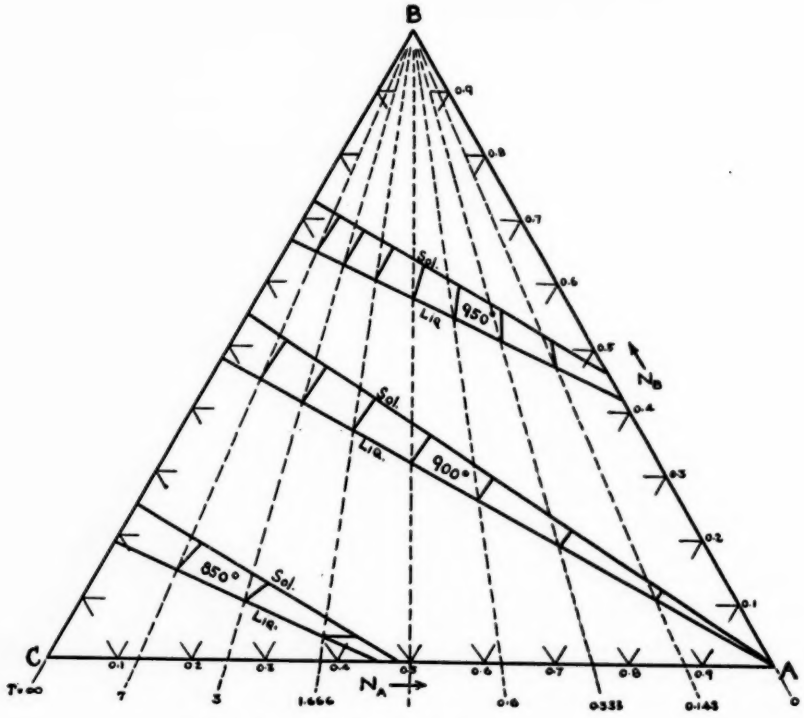

FIG. 1. Isotherms for an ideal ternary system.

Since an infinite number of tie-lines exist at a given temperature, another condition must be fixed before these equations can be solved. The most satisfactory treatment is to derive an equation for the mol fraction of one component with a fixed ratio of the mol fractions of the other two. Thus, in deriving an equation for N_B we shall assume a fixed value r for N_C/N_A, whence,

$$N_C = rN_A, \quad N_B + N_A + rN_A = 1. \tag{7}$$

From Eqs. (5) and (6)

$$N_B k_B e^{\Delta H_B/RT} = 1 - N_A' - N_C'$$

and

$$N_B k_B e^{\Delta H_B/RT} = 1 - N_A k_A e^{\Delta H_A/RT} - N_C k_C e^{\Delta H_C/RT}$$

and with Eqs. (7)

$$N_B = \frac{(1+r) - k_A e^{\Delta H_A/RT} - rk_C e^{\Delta H_C/RT}}{(1+r)k_B e^{\Delta H_B/RT} - k_A e^{\Delta H_A/RT} - rk_C e^{\Delta H_C/RT}}. \tag{8}$$

Introducing convenient values of r, the mol fractions of "B" for the liquidus surface can be calculated for the temperature range of the system. It will be noted that when r is set equal to 0 or ∞, corresponding to the binary systems $B-A$ and $B-C$, Eq. (8) reduces to the form of Eq. (1). To fix the composition of the solid phase in equilibrium with this liquid phase of mol fraction N_B and ratio r at the temperature T, the mol fractions of two components must be calculated, since in general the solidus will not lie on the same ratio line as the liquidus.

These values are readily calculated, however, from Eqs. (5) and (7), whence,

$$N_B' = N_B k_B e^{\Delta H_B/RT},$$
$$N_A' = ((1-N_B)/(1+r))k_A e^{\Delta H_A/RT}. \tag{9}$$

It is obvious that Eqs. (8) and (9), calculating along a series of convenient constant ratio lines, will serve to establish liquidus and solidus surfaces over the entire range of temperature and to fix the tie-line for each liquid-solid equilibrium.

TABLE I.

A	B	C
$\Delta H_A = 2500$	$\Delta H_B = 3000$	$\Delta H_C = 2000$
$T_A = 900$	$T_B = 1000$	$T_C = 800$
$k_A = 0.2478$	$k_B = 0.2213$	$k_C = 0.2848$

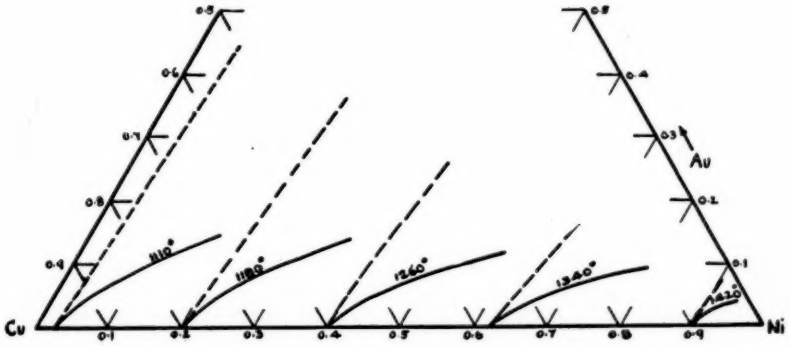

FIG. 2. Liquidus isotherms for the Ni–Cu–Au system. Dotted line, ideal; solid line, experimental.

These equations can be applied to an hypothetical example to illustrate the forms of isothermal sections for an ideal system. We shall assume the following data (Table I) for the components A, B and C, in which the heats of fusion are in calories/mol and the melting points in degrees absolute.

In Table II the calculated values of N_B, N_B' and N_A' are shown for various "r" values at three temperatures, and in Fig. 1 the corresponding liquidus and solidus curves and tie-lines are shown on the usual type of ternary diagram section.

TABLE II.

$r=N_C/N_A$	∞	7	3	1.666	1.0	0.6	0.333	0.1428	0
950°K									
N_B	0.662	0.643	0.622	0.597	0.573	0.543	0.504	0.466	0.420
N_B'	0.722	0.700	0.678	0.651	0.625	0.592	0.550	0.508	0.457
N_A'	—	0.042	0.088	0.141	0.200	0.267	0.349	0.437	0.543
900°K									
N_B	0.480	0.447	0.409	0.364	0.316	0.257	0.185	0.102	0
N_B'	0.548	0.510	0.466	0.416	0.361	0.293	0.212	0.117	0
N_A'	—	0.069	0.148	0.238	0.342	0.464	0.612	0.786	1
850°K									
N_B	0.189	0.144	0.095	0.038	—	—	—	—	—
N_B'	0.247	0.188	0.123	0.039	—	—	—	—	—
N_A'	—	0.116	0.246	0.392	—	—	—	—	—

THE COPPER-NICKEL-GOLD SYSTEM

The binary system of copper and nickel, as previously shown,[1] gives practically an ideal liquidus curve. It is of interest to consider the departure from ideal behavior on the addition of a third component. The liquidus isotherms for the ternary system of copper, nickel and gold have been determined.[3] These results have been recalculated to a mol fraction basis and are plotted as full lines at several temperatures in Fig. 2. The dotted lines are the ideal liquidus curves calculated from Eqs. (8) and (9), with the melting points of Ni, Cu and Au, 1450°C, 1083°C and 1065°C, and the heats of fusion per gram atom, 4280 cals., 2655 cals., and 3130 cals., respectively. It is apparent that marked deviations occur at relatively low mol fractions of gold, as would be anticipated, since the gold-nickel system shows partial miscibility in the solid state and the gold-copper system, though completely miscible in the solid state, shows a minimum in its phase diagram.

[3] De Cesaris, Gazetta Chemica Italiana **44**, 1, 27, 14.

Electronic Structures of Polyatomic Molecules. VII. Ammonia and Water Type Molecules and Their Derivatives

ROBERT S. MULLIKEN, *Ryerson Physical Laboratory, University of Chicago*

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Spectroscopic and ionization potential data are used in obtaining electron configurations in terms of molecular orbitals for NH_3, PH_3, H_2O, H_2S and their derivatives, e.g., CH_3NH_2, $(CH_3)_2NH$, N_2H_4, H_2O_2, CH_3OH, NH_2Cl, ClOH, Cl_2O. These electron configurations hold for molecules in their normal states, but can be used in predicting the energy of "vertically" excited states, i.e., energies corresponding to nuclear dimensions the same as for the normal state. Frequent close similarities between the spectra of parent molecules and their derivatives are explained (also the similarities between alkyl halides such as CH_3I, C_2H_5I, etc.). Estimates of vertical ionization potentials for the various orbitals used are given. Various points (types of orbitals used, Rydberg series, predissociation) are touched on. The longest wavelength ultraviolet spectra and minimum ionization potential are attributed in the NH_3 derivatives to excitation of a nearly nonbonding electron of the N atom, in the H_2O and H_2S derivatives to excitation of a nonbonding O or S atom electron. (Exception: compounds containing I, Br, and perhaps Cl, where the halogen atom supplies the most easily excited and ionized electron.)

I. AMMONIA DERIVATIVES

IN a recent paper,[1] conclusions concerning electronic structures and their relations to ultraviolet spectra and ionization potentials were summarized for certain methane derivatives, particularly those of the CH_3X type (X = halogen). A similar summary is given here for derivatives of NH_3, H_2O, and of analogous molecules such as PH_3, H_2S. The structures are expressed in terms of electron configurations, using atomic orbitals for unshared electron configurations, molecular orbitals of various types for shared electrons.[2, 3]

The normal state of NH_3 (pyramidal form, symmetry C_{3v}), omitting the N atom 1*s* electrons, may be described[2] as:

$$[sa_1]^2[\pi e]^4[za_1]^2, {}^1A_1, \qquad (1)$$

	N	NH_2	N
Appr. loc.			
Vert. I	(27)	(16)	11.

Symbols a_1, e, and A_1 are systematic classification symbols,[1, 2] appropriate to symmetry C_{3v}. Symbols s, π, z are particular symbols briefly descriptive of the orbital in question. The orbital $[sa_1]$ is primarily an N atom 2*s* orbital, shared a little by all three H atoms,[2] and so contributes a little to all three N−H bonds. The pair of orbitals $[\pi e]$ is degenerate; they have forms which might in rough approximation be built up from N atom $2p\pi$ (i.e., $2p_x$ and $2p_y$) combined with H atom 1*s* orbitals; they give strong N−H bonding. The main bonding characteristics and approximate locations of the various orbitals are summarized under the configuration (1).

The orbital $[za_1]$ is roughly just a $2p\sigma$ (i.e., $2p_z$) *nonbonding* orbital of the N atom. The pure $2p_z$ form (z axis = axis of symmetry of NH_3) is, however, somewhat modified in a way which can be roughly described as by admixture of $2s_N$ and of 1*s* of the three H's, and contributes a little to the three N−H bonds. The observed ionization potential I (11.1 volts) of the NH_3 molecule can safely be identified as the I (= term value) of $[za_1]$. This value may be compared with the value 12.2 volts approximately predicted for the vertical I of a nonbonding $2p_z$ by methods described in an earlier paper.[3] (This prediction supersedes one[2] made by less adequate methods.) The agreement is as good as is found in other cases.[1, 3] Part of the discrepancy may be accounted for by a lack of complete verticality in the observed I. ("Vertical" or Franck-Condon I corresponds to ionization without change in molecular dimensions; "adiabatic" I, i.e., minimum I allowing readjustment of molecule to new equilibrium, is necessarily less, although the difference should be very small for I of a com-

[1] R. S. Mulliken, Phys. Rev. **47**, 413 (1935). Strongly supported by results of W. C. Price, Phys. Rev. **47**, 419, 510 (1935).

[2] *a*. Cf. R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933) and earlier papers. *b*. Also J. Chem. Phys. **3**, 375 (1935), in regard to the general nature of the method (VI of this series). Also in VIII, XI, XII of this series, there are given further details as to the forms of the molecular orbitals indicated here by brief symbols.

[3] R. S. Mulliken, Phys. Rev. **46**, 549 (1934); J. Chem. Phys. **2**, 782 (1934): cf. especially Table IV.

pletely nonbonding electron.) Under the electron configuration (1) are also given estimated vertical I's (semi-empirical method of reference 3) for other orbitals.

Since $[za_1]$ has by far the lowest I (I_{min}) of the orbitals which are occupied in the normal state of NH_3, its excitation should be responsible for the longest wavelength ultraviolet bands. As has been noted before,[1, 2] the frequency at which ultraviolet absorption begins should run approximately parallel to I_{min}.

If we regard the lower excited states of NH_3 as built by adding an electron in an excited orbital to an NH_3^+ core

$$[sa_1]^2[\pi e]^4[za_1],\ ^2A_1 \qquad (2)$$

corresponding to removal of one $[za_1]$ electron from configuration (1), then if we can predict the nature and energies of the possible excited orbitals, we can predict the excited states. It seems probable[2] that all excited orbitals here are nearly like atomic orbitals, forming Rydberg series: $3s$, $4s$, $5s$, $\cdots$ (all of type a_1), $3p\pi$, $4p\pi$, $\cdots$ (type e), $3p\sigma$, $4p\sigma$, $\cdots$ (type a_1), $3d\delta$, $4d\delta$, $\cdots$ (type e), $3d\pi$, $4d\pi$, $\cdots$ (type e), $3d\sigma$, $4d\sigma$, $\cdots$ (type a_1), etc. It may be, however, that some of these series, or at least their lowest members, will show abnormalities because of their relationships to orbitals in the core (cf. the abnormal $y\sigma$ orbitals of He_2).

If the excited orbitals are sufficiently atom-like, $3sa_1$ should be the lowest, giving configuration (3) for the lowest excited states:[2]

$$[sa_1]^2[\pi e]^4[za_1](3sa_1),\ ^3A_1,\ ^1A_1. \qquad (3)$$

The observed ultraviolet absorption bands starting near λ2200 have been attributed already[2] to a transition from (1) to the $^1A_1$ state of (3). Transitions to the $^3A_1$ should be much weaker and displaced probably slightly toward longer wavelengths. The vertical term value of $3sa_1$ can be found approximately by subtracting the excitation potential for the intensity maximum[4a] (about λ1900) of the (1)→(3)$^1A_1$ transition from I of $[za_1]$. The result is about 4.6 volts, a reasonable term value for $3s$ here. Recent work[3a] on the (1)→(3) bands of ND_3 should be mentioned. This indicates that the state (3) and therefore probably the normal state (2) of NH_3^+ has a plane equilibrium form. This is in harmony with suggestions made previously.[2] The absorption observed beginning near λ2300 in PH_3, AsH_3, SbH_3 (wholly continuous in all, except for two diffuse bands λλ2315, 2290 in PH_3)[4] doubtless involves excitation of $[nza_1]$ to $(n+1)sa_1$ just as in NH_3.

In regard to (3), it may be noted that the NH_3^+ core *per se* should be stable, since the electron removed is essentially nonbonding. This does not, however, avert the possibility of predissociation of excited NH_3, which may be thought of as due to interaction of the excited electron with the core in such a way that the former becomes split off together with a hydrogen nucleus of the latter: $NH_3'^+\epsilon \rightarrow NH_2+H$. According to this viewpoint, predissociation should tend to diminish with increase in the principal quantum number of the excited electron. Data on NH_3 and observed Rydberg series in other molecules seem to be in general agreement with this expectation.[4a]

We are now in a position to give a simple explicit reason for the striking similarity which has been observed between the ultraviolet absorption spectra of NH_3 and several of its derivatives, namely, hydrazine (N_2H_4) and several amines (CH_3NH_2, $C_2H_5NH_2$, $C_3H_7NH_2$, $(CH_3)_2NH$, $(CH_3)_3N$).[5] In all of these, absorption begins about λ2300–2500 with a series of more or less diffuse bands and increases in intensity and diffuseness toward the ultraviolet; and the total intensity is about the same in all. It seems strongly improbable that these resemblances are merely superficial or fortuitous, although one should always bear the possibility in mind. The similarity between NH_3, CH_3NH_2, etc., has been explained by Herzberg and Kölsch[5] by saying that excitation is localized in the NH_2 group.

We can now be more specific and attribute the observed absorption in all the foregoing cases to excitation of a nearly nonbonding $[z]$ electron belonging essentially to the N atom,

[3a] W. S. Benedict, Phys. Rev. **47**, 641A (1935).

[4] G. H. Cheesman and H. J. Emeléus, J. London Chem. Soc. 2847 (1932).

[4a] A. B. F. Duncan, Phys. Rev. **47**, 822 (1935): vacuum ultraviolet NH_3 spectrum.

[5] G. Herzberg and R. Kölsch, Zeits. f. Elektrochem. No. 7*b* (1933): amines, etc.; also unpublished photographs of W. C. Price on CH_3NH_2. S. Imanishi, Nature **127**, 782 (1931): hydrazine. Recently, V. Henri and W. Lasareff, Compt. rend. **200**, 829 (1935): methylamine.

and going in each case to a $3s$ excited orbital centered around (although not really belonging exclusively to) the N atom. Thus the excitation is localized around and characteristic of, not the NH_2 group, but rather the trivalent N atom.

This explanation implies that the orbitals $[z]$ and $(3s)$ persist without essential change when H atoms of NH_3 are replaced by substituents (CH_3, etc.), in spite of changes in symmetry. This is entirely reasonable, as we shall see, provided the angles between the three bonds going out from the N atom, and the mean distribution of electricity surrounding the N atom, remain nearly constant. Conversely, from the constancy of the spectrum we have strong support for the constancy of these features of the bonds. An analogous explanation can be applied to the fact[5a] that $P(C_2H_5)_3$ shows absorption in nearly the same region as PH_3.

The structures of the NH_3 derivatives can best be understood by considering first the effect on an NH_3 molecule of a slight displacement of one H atom in such a way as to reduce the symmetry from C_{3v} to C_s. The symmetry group C_s possesses as elements only the identity operation and reflection in a single plane of symmetry through the N and one H atom. Such a distortion splits up any degenerate orbital (type e) of C_{3v}. In this way, $[\pi e]$ of (1) and (2) splits into two orbitals which may be called $[xa'']$ and $[ya']$, where the yz plane passes through the nonequivalent H atom (cf. reference 2, Fig. 1a; also reference 2, Eqs. (2) for approximate forms of $[x]$, $[y]$). Representations a' and a'' are respectively symmetrical and antisymmetrical relative to the plane of symmetry. We then have for NH_3 with symmetry C_s:

$$\underset{\text{N}}{[sa']^2}\underset{\text{NH}_2}{[xa'']^2}\underset{\text{NH}}{[ya']^2}\underset{\text{N}}{[za']^2}, {}^1A'. \qquad (4)$$

The letters under the orbitals indicate approximately the localization or function of the orbitals, e.g., $[x]$ gives bonding between N and two of the H atoms, $[y]$ between N and the third (the displaced one); $[s]$ and $[z]$ are, roughly, nonbonding N atom orbitals, although more precisely they give some bonding to all three H's, almost equally to all.

Electron configurations can now be written for various derivatives of NH_3. In NH_2X, for example (X = halogen), X is substituted for the displaced H, and $[y]$ takes on the burden of the N–X bond, while $[x]$ remains practically unchanged; $[s]$ and $[z]$ are nearly unchanged, except that they participate slightly in the N–X and the two N–H bonds, instead of in three N–H bonds as in NH_3. In considering the spectrum of NH_2X, the nonbonding $np\pi_X$ electrons may be of importance, just as in CH_3X,[1] because of their low I values. The case is, however, somewhat different from CH_3X in that here the central atom N is able to furnish an electron $[za']$ of I low enough to compete with I of $np\pi_X$. Study of the I data for $np\pi_X$ in CH_3X indicates, however, that I_{min} in NH_2X also is probably I of an $np\pi_X$, except in NH_2F and possibly NH_2Cl. The next lowest I is then that of $[z]$ of the N atom.

For CH_3NH_2 a good electron configuration can easily be written down from a comparison of those of CH_3X and of XNH_2. The result is:

$$\underset{\text{N}}{[sa']^2}\underset{\text{CH}_2}{[sa']^2}\underset{\text{NH}_2}{[xa'']^2}\underset{\text{CH}_2}{[xa'']^2}\underset{\text{CH}}{[ya']^2}\underset{\text{NC}}{[ya']^2}\underset{\text{N}}{[za']^2}, {}^1A' \qquad (5)$$

approx. location	N	CH_2	NH_2	CH_2	CH	NC	N
est. I	(27)	(22)	16		14.5	13.5	11.

Formulation (5) applies to the probable equilibrium arrangement of the atoms, with C–N–H and H–N–H bond angles similar to the H–N–H angles in NH_3. Free rotations around the C–N bond will, of course, upset this and will spoil the rigorous symmetry C_s, leaving, however, an approximate local symmetry C_{3v} within the CH_3 group and C_s within the NH_2. Nevertheless this does not really mean any serious alteration in the orbitals given in (5), but only some changes in their technical classifications.

In (5) we really have, essentially, the orbitals

[5a] H. W. Thompson and J. J. Frewing, Nature **135**, 507 (1935): ethyl and methyl derivatives of NH_3, PH_3, H_2O, H_2S; etc.

$[sa_1]$ and $[\pi e]$ of the CH_3 radical (C_{3v}), but technically, for the equilibrium arrangement, $[\pi e]$ is slightly split up into $[xa'']$ and $[ya']$ in accordance with the total symmetry C_s. These orbitals $[\pi e]$ are nevertheless expected to be practically the same as in CH_4 or in CH_3X, and should have nearly the same I as in those molecules (cf. discussion of $[\pi e]$ in CH_3X in reference 1). Similarly, we have $[xa'']$ of NH_2 and $[za']$ of N nearly the same as in NH_3 or NH_2X, and $[sa']$ not far different than in NH_2X or NH_3. Finally we have $[ya']$ which in LCAO approximation[2b] is of the form $[(2p_y)_N+2p\sigma_C]$. This links the C and N and is intermediate in character between the C−C bonding orbital $[\sigma+\sigma, a_1]$ of C_2H_6 (symm. D_3, similar to C_{3v}, see IX of this series) and the N−N bonding orbital $[y]$ of N_2H_4 (see Eq. (6) below), of LCAO form $(2p_y+2p_y)$.

Strictly speaking, the orbitals of CH_3NH_2 cannot be quite so much localized as (5) would indicate. There is necessarily some interaction and mixing between all indicated orbitals of type a', and again between all those of type a''. In particular, the orbitals $[sa']_{NH_2}$ and $[sa']_{CH_3}$ must both participate somewhat in the C−N bond, as one sees for instance by noting that $[s]$ in CH_4 participates in all four bonds, $[s]$ in NH_3 in all three bonds. Nevertheless (5) represents about the best simple system of orbitals that one can assign, and in the writer's opinion probably corresponds fairly well to the true situation. The similarity of the CH_3NH_2 to the NH_3 longest wavelength ultraviolet absorption is rather satisfactory empirical evidence that orbital $[za']_N$ is nearly the same in CH_3NH_2 as in NH_3, in spite of the fact that some mixing with other orbitals of type a' must exist. In particular, one would not have been surprised to find strong mixing between $[za']_N$ and $[ya']_{NC}$, hence a pronounced change in forms of the orbitals with the changed symmetry. The spectroscopic evidence that this effect is not important gives us considerable assurance that other possible mixings among the approximate orbitals indicated in (5) can also tentatively be neglected. The existence of free rotation (if it is a fact here) also indicates lack of strong interactions between $[\pi e]$ of CH_3 and the orbitals of NH_2. Other evidence indicating lack of interaction between such nearly non-overlapping orbitals of different radicals will be cited in VIII of this series.

The foregoing discussion indicates that in setting up electron configurations for complex molecules, one can often with some assurance assume close resemblance between orbitals of derivative and parent molecules, even when rigorous symmetry considerations fail one. (Most derivatives are relatively complex and lacking in rigorous symmetry.) This principle must, however, be used with caution. It cannot be expected to apply in extreme cases where bond angles or bond strengths depart markedly from those of the parent molecules.

In connection with the foregoing principle, it is found that, even though we start with the idea of using nonlocalized orbitals, approximate localization often occurs automatically, e.g., $[z]$ in NH_3 derivatives apparently remains approximately localized as in NH_3 in spite of opportunities for mixing with other orbitals to form nonlocalized resultants. In our discussion of CH_4 and NH_3 derivatives (reference 1 and here) we have arrived quite naturally at electron configurations containing not only highly localized (atomic) orbitals, but also two kinds of semi-localized orbitals: (1) "*radical*," i.e., intra-radical, orbitals, e.g. $[s]$ of CH_3 and NH_2, $[\pi]$ of CH_3, $[x]$ of NH_2; and (2) inter-radical orbitals, e.g., $[y]$ of the C−N bond in CH_3NH_2 or of the N−X bond in XNH_2. Radical orbitals are nonlocalized with respect to a radical but localized so far as the molecule as a whole is concerned. In some cases, as $[\pi]$ of CH_3 in CH_3NH_2 or CH_3X, this localization is largely automatic; in others, e.g. $[s]$ of CH_3 or NH_2, which tend to mix with the inter-radical bonding orbital, we impose localization in part arbitrarily for the sake of simplicity, in the same way that we use atomic orbitals for electrons of two atoms in a molecule when such orbitals can be so chosen as not to interact very much. As for inter-radical orbitals, which usually giving inter-radical bonding in the case of normal states, these often tend automatically to be largely localized in the region of the bond, although this is by no means always the case.

Returning now to CH_3NH_2, we notice that in order that this may give an absorption spectrum closely resembling that of NH_3, it is necessary

not only that $[za']$ in (5) shall be nearly the same as in NH_3 but also that the excited orbital $3s$ shall be nearly the same in both. [Conceivably, of course, both $[za']$ and $3s$ could be different than in NH_3, yet give a very similar spectrum, but this is improbable.] It is important to note that the orbital $3s$ is so large (estimated effective radius about 2.6×10^{-8} cm) as partly to overlap the CH_3 group (N−H and C−H distances each about 10^{-8} cm, C−N distance about 1.5×10^{-8} cm). Hence it cannot be considered as localized on the N atom. Nevertheless, since the excited electron $[za']$ has come out of the N atom, the center of attraction for the $3s$ is located near the N nucleus, both in NH_3 and in CH_3NH_2 and likewise in $(CH_3)_2N$, $C_2H_5NH_2$, and other amines. This is probably sufficient to permit the needed close similarity of the excited orbital in all these cases.

Following the line of approach indicated above, it is possible to write reasonable electron configurations for $(CH_3)_2NH$, $(CH_3)_3N$ and others. In doing so, complications arise because of variations in symmetry and for other reasons. Some of the complications, such as changes in technical classification of orbitals depending on symmetry, small splittings-up of orbitals which in cases of high symmetry (as e.g. in parent molecules) are degenerate, are more apparent than real. In other words, conspicuous changes in rigorous technical designations of orbitals often correspond to relatively trivial changes in actual forms of orbitals. This is illustrated in the difference between (1) and (4).

As another example of NH_3 derivatives, we may consider the hydrazine molecule (N_2H_4). The molecule as a whole is probably totally lacking in symmetry,[6] so that no classification of orbitals is possible as regards symmetry type. The normal state, omitting inner $1s$ N atom electrons, may be described as

$[s]^2$	$[s]^2$	$[x]^2$	$[x]^2$	$[y]^2$	$[z]^2$	$[z]^2, {}^1A$	(6)
N_A	N_B	N_AH_2	N_BH_2	N_AN_B	N_A	N_B	
27	27	16	16	15	11	11	.

N_A and N_B refer to the two N atoms. More or less mixing must occur between the orbitals indicated. In particular, resonance must occur between the members of each pair of like-designated orbitals, e.g., $[z]_A$, $[z]_B$, so that each such pair must be represented by a pair of I values. Approximately, however, these resonance and other effects, and the resulting splitting up or other changes of I values, may probably be neglected, in the same way that we neglect the resonance between, e.g., the $1s$ nitrogen non-bonding atomic orbitals which are tacitly part of (6).

The similarity of the N_2H_4 to the NH_3 spectrum is then accounted for, provided $3s$ is nearly as in NH_3. Actually, resonance between $3s_A$ and $3s_B$ can surely not be neglected, since these would overlap very strongly. Instead of $3s_A$ and $3s_B$ we must then have two new forms roughly like $a(3s_A+3s_B)$ and $a'(3s_A-3s_B)$. However, one finds that the former of these will be not very different from a $3s$ orbital centered about a point half-way between the two N nuclei and so is probably nearly enough like $3s$ of NH_3 to fill our need.

II. Derivatives of Water and Hydrogen Sulphide

The electron configuration for the normal state of H_2O (symmetry C_{2v}, z axis = symmetry axis, x axis = perpendicular to HOH plane) can be written, omitting inner-shell electrons, as follows:[1]

$$(2sa_1)^2[yb_2]^2\,[za_1]^2(2xb_1)^2, {}^1A_1 \quad (7)$$

approx. location	O	HOH	HOH	O	
I_{vert} =		(32)	(18)	(17)	12.7 .

The orbitals $2s$ and $2x$ (i.e., $2p_x$) are essentially nonbonding O atom orbitals, while $[y]$ and $[z]$ both participate in both O−H bonds. Estimated vertical I's are given below. The value 12.7 volts for $2x$, however, is an observed value from electron impact data.[7] Another value of 12.9 volts is obtained from the edge of a strong continuous absorption in the far ultraviolet,[8] which probably represents approximately the convergence point of Rydberg series involving excitation of $2x$. Absorption continua[8] with fairly well marked long wavelength edges at 16.7 ± 0.5 and 17.8 ± 0.5 volts may similarly

[6] Cf. W. G. Penney and G. B. B. M. Sutherland, J. Chem. Phys. **2**, 492 (1934).

[7] H. D. Smyth and D. W. Mueller, Phys. Rev. **43**, 116 (1933).

[8] G. Rathenau, Zeits. f. Physik **87**, 32 (1933).

correspond to the estimated I's for $[y]$ and $[z]$. The I observed at about 16 volts by electron impact[7] doubtless also corresponds to $[y]$ or $[z]$ or both. In this connection it should be recalled that the observed minimum I's obtained from Rydberg series or their limiting continua are adiabatic I's and should always be smaller than estimated vertical I's in the case of bonding electrons (e.g., $[y]$, $[z]$). In the case of electron impact I's and adiabatic I's, values varying between vertical I's and adiabatic I's may perhaps be obtained depending on the delicacy of detection.

The observed minimum I of H_2O of about 13 volts, attributed to the nonbonding $(2xb_1)$, may be compared with the value 14.7 volts approximately predicted for a nonbonding $2p_x$ of oxygen by the methods earlier described.[3] As in the case of the nonbonding orbitals $[za_1]$ of NH_3 and $(np\pi_1)$, etc., of CH_3I, etc., the observed value is somewhat less than the predicted.

As lowest excited states of H_2O one might expect

$$(2sa_1)^2[yb_2]^2[za_1]^2(2xa_1)(3sa_1),\ ^{3,1}A_1. \qquad (8)$$

The observed continuum starting rather sharply at 6.9 volts (λ1780) and having its maximum at about 7.5 volts may be reasonably attributed to transitions to the $^1A_1$ of (8), with much fainter transitions to the $^3A_1$. This interpretation gives a reasonable vertical term value (I=about $12.7-7.5=5.2$ volts) for $3s$. The fact that the transition gives continuous absorption must be attributed to predissociation, apparently into $O(p^4, {}^1D)+H_2({}^1\Sigma^+_g)$.[9, 12]

The molecule H_2S should have normal and lowest excited configurations analogous to (7) and (8), but with quantum numbers one greater ($3sa_1$, $3xb_1$, $4sa_1$, etc.) and with smaller I's. The observed minimum I of H_2S (10.4 volts according to electron impact data[10] and about 10.42 volts from Rydberg series found by Price[11]) undoubtedly is a nearly vertical I corresponds to removal of a $(3xb_1)$ nonbonding electron. Although Price reports two very slightly different Rydberg series limits, it is clear that there can be only one insofar as electronic energy is concerned.

The molecules H_2S, H_2Se, H_2Te all show absorption continua[12] attributable to a transition $(nx)\rightarrow(n+1)s$ like the first ultraviolet continuum of H_2O. These continua are displaced toward longer wavelengths with increasing molecular weight (first absorption maximum at about 7.5, 6.2, 5.9 volts for H_2O, H_2S, H_2Se). The position of the maximum, combined with I, gives for H_2S a reasonable vertical term value for the excited orbital $4sa_1$. The value is $10.4-6.2=4.2$ volts, compared with 5.2 for $3s$ in H_2O.

Just as the longer wavelength ultraviolet spectra of NH_3 derivatives resemble closely those of NH_3, so we might expect similar resemblances between H_2S and H_2O derivatives and the respective parent molecules. Likewise the minimum I of such derivatives would be expected, provided complications (e.g., atoms like I or Br containing nonbonding electrons of lower I) are absent, to be that of the nonbonding (x) orbital and roughly the same as in the parent molecule. Price[11] predicts that I will decrease somewhat as alkyl groups are substituted for H atoms in H_2S or H_2O. Available spectroscopic data[5a, 11, 13, 16, 19] tend to support the foregoing expectations.

Electron configurations of H_2O derivatives can be set up, as in the case of CH_4 and NH_3 derivatives, by starting from a distorted H_2O molecule, here a symmetry C_s, obtained by displacing one H atom slightly. This gives instead of (7),

$$(2sa')^2[ya']^2[za']^2(xa'')^2,\ ^1A'. \qquad (9)$$

Orbitals $[y]$ and $[z]$ now belong to the same representation and can mix. Since they are probably of nearly equal energy in H_2O or H_2S (cf. XII of this series), they may mix rather strongly if the distortion is made large, or if one H is replaced by another atom or radical making the strengths of the two bonds decidedly different. Mixing between $[y]$ and $[z]$ is equivalent to a rotation of axes. The extreme of mixing

[9] M. Kimura, Sci. Papers Inst. Phys. Chem. Res. **18**, 150 (1932).
[10] C. A. MacKay, Phys. Rev. **24**, 319 (1924).
[11] W. C. Price, J. Chem. Phys. **3**, 256 (1935); Bull. Am. Phys. Soc. **10**, 9 (1935). The writer is greatly indebted to Dr. Price for an opportunity to see these in manuscript form, as well as for other unpublished data.
[12] C. F. Goodeve and N. O. Stein, Trans. Faraday Soc. **27**, 359–572 (1931).
[13] H. Ley and B. Arends, Zeits. f. physik. Chemie **B15**, 311 (1932): H_2S and its alkyl derivatives.

would be represented by two new orbitals $[y'a']$, $[z'a']$ with axes y', z' directed (for a 90° bond angle) along the two bonds, and differing by 45° from the axes of $[y]$ and $[z]$. The nonbonding orbital (xa''), belonging to a different representation a'' (antisymmetrical to the symmetry plane) is not affected by any such mixing or rotation of $[y]$ and $[z]$.

A molecule like ClOH would be represented by (9), plus nonbonding electrons of Cl, particularly the group $(3p\pi)_{Cl}{}^4$, whose I should be near and probably less than that of (xa''). Spectra of HOCl and HOBr in water solutions are known.[14] The absorption is continuous, beginning near λ3300 and increasing fairly steadily. The HOBr absorption curve is displaced about 0.4 volt toward longer wavelengths as compared with HOCl.

Cl_2O (symmetry C_{2v} like H_2O) should be represented by (7) plus two sets of $(3p\pi)_{Cl}{}^4$. The fact that Cl_2O shows continuous absorption throughout the visible and ultraviolet[15] (with maxima near λλ6300 (weak), 5800 (weak), 4300, and 2500 (strong) seems, however, difficult to reconcile with such an electron configuration. The longer wavelength absorption has been shown to produce dissociation into O+ClO.[15]

The apparent discrepancy with our expectations may perhaps be reconciled somewhat as follows: (1) It should be clearly noted that our theory considers primarily only *vertical* processes of ionization and excitation (molecular dimensions constant). (2) Although an absorption maximum is usually a guarantee of vertical excitation (hence our continual use of the energies of absorption maxima, not of long wavelength edges), this may not always be true for weak maxima, such as those at λλ6300, 5800, 4300. It may be that these maxima represent vertical excitation with respect to certain coordinates, e.g., the Cl−O distances, but not with respect to all, e.g., perhaps not for the Cl−O−Cl angle. (3) For a linear (or otherwise altered) Cl−O−Cl it is perfectly possible that the electron configuration and I values would be greatly altered as compared with (7). Hence if the weak maxima represent transitions which are partially oblique (i.e., nonvertical, or anti-Franck-Condon) it is in principle quite possible to account for the necessary low energy excited electron states. (4) As a side-light it is worth noting that in some sense, or in some degree, it is impossible to draw a sharp line in polyatomic molecules between nonvertical processes with continuous absorption, and predissociation processes.

The foregoing discussion is important in showing that our present approach needs to be greatly extended (by a study of electron configurations and vertical I values for every conceivable configuration of nuclei) in order to permit a complete account of the electronic states and spectra of polyatomic molecules. Nevertheless the present approach should represent a good beginning, especially when nonbonding electrons are excited to high (Rydberg) levels, or are ionized.

For CH_3OH (symmetry C_s, or none, with C−O−H bond angle presumably nearly like the H−O−H angle in H_2O) we might have

$$(2s)^2[s]^2\,[z']^2[y']^2[\pi]^{2+2}(2x)^2,\ {}^1A \qquad (10)$$

approx. location	O	CH_3	OH	OC	CH_3	O
est. I	32	22	17.5	16	14.5	12.5

Here $[s]$ and $[\pi]$, the latter here really split into two orbitals differing slightly in energy, belong essentially to CH_3, $(2s)$ and $(2x)$ to O, while $[z']$ and $[y']$ together give the O−H and O−C bonding. Formula (10) is written corresponding to the extreme y', z' orientation of axes, localizing the O−H bonding in $[z']$ and the C−H bonding in $[y']$. The actual orbitals must, however, be mixtures of these extreme forms, although very likely the mixing may not be strong. At any rate, $(2x)$ should probably be practically free from mixing and should have the lowest I. Ultraviolet absorption of CH_3OH begins near λ2000, and is continuous, with the first maximum at about 6.9 volts (cf. H_2O, 7.5 volts).[16] C_2H_5OH shows a very similar absorption.[16] It is reasonable to suppose that this absorption has the same explanation (transition

[14] K. Schaefer, Zeits. f. physik. Chemie **93**, 312 (1919).
[15] Cf. Goodeve and Wallace; and W. Finkelnburg, H. J. Schumacher and G. Stieger, Zeits. f. physik. Chemie **B15**, 127 (1931).
[16] G. Herzberg and G. Scheibe, Zeits. f. physik. Chemie **B7**, 390 (1930).

$2x \rightarrow$ probably $3s$) in CH_3OH and C_2H_5OH as in H_2O. A similar statement applies to the quite similar continua of $(CH_3)_2O$ and $(C_2H_5)_2O$ with maxima at about 6.5 volts.[16, 11] Similar relations hold between the absorption spectra of H_2S, C_2H_5SH, $(CH_3)_2S$, etc.[13] The situation resembles that for NH_3, CH_3NH_2, $C_2H_5NH_2$, $(CH_3)_2NH$, etc., although there the presence of discrete bands makes the argument more certain.

For NH_2OH one might now expect:

NH_2OH (*no symm.*):

$$(2s)^2[s]^2[z']^2[y']^2(2x)^2(z)^2, {}^1A, \quad (11)$$
$$\begin{array}{cccccccc} & O & N & OH & ON & O & N & \\ & 32 & 27 & 17.5 & 17 & 13 & 11.5 & \end{array}$$

modified by more or less mixing between $[z']$ and $[y']$. NH_2OH is reported to be transparent even in concentrated solutions at least to about $\lambda 2200$.[17] This is reasonably in harmony with our expectations.

For H_2O_2,[6] we may write:

H_2O_2 (*no symm.*):

$$(2s)^2(2s)^2[y']^2[z']^2[z']^2(2x)^2(2x)^2, {}^1A, \quad (12)$$
$$\begin{array}{cccccccc} O & O & OO & OH & OH & O & O & \\ & 32 & & 18 & 17.5 & & 13 & \end{array}$$

modified by more or less mixing and resonance between the approximate orbitals indicated. The observed absorption spectrum of H_2O_2 is a continuous one increasing steadily in intensity from $\lambda 3750$ (2.3 volts) to at least $\lambda 2150$ (5.75 volts) and producing dissociation into two OH both in their normal state $^2\Pi$ at the longer, and into one $^2\Pi$ and one excited $^2\Sigma^+$ at the shorter wavelengths.[18] The long-drawn-out absorption extending to long wavelengths may be due to nonvertical excitation processes (cf. discussion of Cl_2O). Since the first maximum of absorption evidently comes below $\lambda 2150$, and may come near that of H_2O, it is quite possible that for vertical excitation, the lowest energy excitation process is $2x \rightarrow 3s$ as in H_2O. (Of course $3s$ here must be centered between the two O atoms, not around one; cf. discussion of N_2H_4 above.)

Another possibility which should be considered is that $3s$ is not the lowest vertically excited orbital here. The O–O bonding orbital $[y']$ in (12) is really of the LCAO form $(2p_{y'}+2p_{y'})$, and there should be a corresponding excited orbital $(2p_{y'}-2p_{y'})$ which may be fairly low in energy here: cf. the analogous orbitals $(np\sigma+np\sigma, \sigma_g)$ and $(np\sigma-np\sigma, \sigma_u)$ which are, respectively, the bonding and the lowest excited orbital in the halogen molecules X_2.[3] Possibly the longer wavelength absorption in H_2O_2 is due to a weak transition $(2x) \rightarrow (2p_{y'}-2p_{y'})$. A similar possibility may be involved in ClOH and other cases (even Cl_2O).

Something analogous also would also seem possible in N_2H_4, NH_2Cl, NH_2OH. The N–N bonding orbital $[y]$ in N_2H_4 in (6) is of LCAO form $[p_y+p_y]$, like $[y']$ of H_2O_2 in (12), and there should be an excited orbital $[p_y-p_y]$ which might be of low energy. The spectra, however, do not indicate the existence of any excited orbital of lower energy than would be reasonable for $3s$. It must be admitted that our conclusions as to low excited orbitals are in many cases still very tentative. The normal state configurations are much more certain.

III. Alkyl Halides

In conclusion, it is of interest to return, in the light of the foregoing discussion, to certain molecules mentioned in a previous article.[1] It is found that there is an extraordinary similarity between the ultraviolet absorption spectra of all alkyl iodides (CH_3I, C_2H_5I, C_3H_7I, etc.) down to $\lambda 1500$ at least.[16, 11, 20] Each has a continuum near $\lambda 2600$ (upper level A) and a pair of band systems, closely similar to each other, near $\lambda 1900$ (upper levels B and C). The systems involving B and C differ in the heavier alkyl iodides as compared with CH_3I mainly just in having a more complex fine structure. This is presumably due to a small splitting-up of degenerate orbitals by reduction in symmetry, or to added vibrational degrees of freedom, or both. Also in some of the heavier iodides the bands are more diffuse and the C component lacking, very likely because of predissociation.

The close similarities among the various alkyl iodide spectra remind one of those noted above among the various alkylamine spectra (CH_3NH_2,

[17] Baly and Desch, J. London Chem. Soc. **93**, 1747 (1908).
[18] H. C. Urey, L. H. Dawsey and F. O. Rice, J. Am. Chem. Soc. **51**, 1371 (1929).
[19] G. Scheibe, F. Povenz and C. F. Linström, Zeits. f. physik. Chemie **B20**, 283 (1933); R. A. Rehman, R. Samuel and Sarf-ud-Din, Ind. J. Phys. **8**, 537 (1934).
[20] W. C. Price, J. Chem. Phys. **3**, 365 (1935): ethyl halides, with their I's.

$C_2H_5NH_2$, etc.) and between CH_3OH and C_2H_5OH, and they probably have a similar explanation. It has been shown[1] that the A, B and C levels of CH_3I all result from excitation of a nonbonding $5p\pi$ I atom electron out of a closed group $5p\pi^4$, the energy interval $C-B$ agreeing with that to be expected for $^2\Pi_{\frac{1}{2}}-{}^2\Pi_{1\frac{1}{2}}$ of the group $5p\pi^3$ of I. The same explanation is applicable to the other alkyl iodides (C_2H_5I, etc.).

In order to account for the almost identical position, in all these iodides, of the spectra leading to these excited levels, it is necessary that the excited orbitals involved should be nearly the same in all (cf. our discussion of the NH_3 derivatives). It would be plausible to suppose that, since the excitation takes place in the I atom leaving the latter as a positively charged center, the excited orbital also is localized around this atom. The simplest assumption would be that in the A level the excited orbital is $6s$ of iodine, in the B and C levels it is another iodine orbital, perhaps $6d\pi$. (Certain features of the CH_3I bands make it probable that the excited orbital is of the e type (to which $6d\pi$ belong) in the B, C, levels.) Both these orbitals would be large and would overlap the neighboring atoms but should not be much altered by the change from CH_3I to C_2H_5I, etc. In the previous article,[1] other suggestions as to the excited orbitals were made, according to which they were ascribed to the region of the C–I bond or of the CH_3 group in CH_3I. It is probably best to leave the question of the exact nature of the excited orbitals open for the present, except that on the basis of the spectra it seems clear that they are localized *near* the I atom.

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Electronic Structures of Polyatomic Molecules. VIII. Ionization Potentials

ROBERT S. MULLIKEN, *Ryerson Physical Laboratory, University of Chicago*

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Observed and predicted values for ionization potentials of nonbonding electrons are compared, and the differences attributed mainly to charge-transfer effects. Multiplet interval and other criteria are cited as evidence that assumed nonbonding orbitals are really such, i.e., that they are effectively localized and interact little with other orbitals. The prediction of ionization potentials for bonding and antibonding electrons is also discussed. The present paper grows, in part, from suggestions of Price as to the effects of dipole fields on ionization potentials.

I. NONBONDING ORBITALS

IN pursuing a program[1, 2, 3, 4] of describing molecular electronic structures in terms of electron configurations, it is of considerable importance to be able to make approximate predictions as to the ionization potentials (I) corresponding to various types of orbitals in molecules. Methods for doing this were outlined in previous papers.[5] Since a considerable body of empirical data has now accumulated on observed I's, it appears desirable at this point to see what conclusions can be drawn from a comparison between these and predicted I's. This will make possible a refinement of our I predictions, and will be found important in helping us reach definite conclusions as to electron configurations.

We shall first consider orbitals which are essentially nonbonding, since for these the predicted I's (of the type I*)[5] are much more

[1] R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935): VI of this series.
[2] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933): V.
[3] R. S. Mulliken, Phys. Rev. **47**, 413 (1935).
[4] R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935): VII.
[5] R. S. Mulliken, Phys. Rev. **46**, 551 (1934); J. Chem. Phys. **2**, 789–793 (1934). See also J. Savard, J. de phys. et rad. [VII] **4**, 650; **5**, 27 (1934), and elsewhere.

* In examining Table I, one should bear in mind that the predicted I values for Br and I are somewhat uncertain because of lack of complete spectroscopic data on the atoms; also that observed I values obtained by electron impact methods (unstarred in the table) are likely to be appreciably in error; and finally that the observed I values may

TABLE I. *Observed and predicted I's for nonbonding electrons.*

Atom	Electron ionized Type	Pred. I	A_2	Observed I for H_nA	CH_3A	C_2H_5A
I	$5p\pi$	10.85	10.0	12.75	9.49†	9.30†
Br	$4p\pi$	12.28	12.8	13.25	10.49†	10.24†
Cl	$3p\pi$	13.62	13.2	13.75, 12.9	11.17†	10.8†
S	$3p_x$	10.83		10.42†		
O	$2p_x$	14.73		12.7		
N	$2p_z$	12.24		11.1		

Notes. Predicted I's are I^*'s obtained by method of Ref. 5; in the case of sulfur, data from J. Ruedy, Phys. Rev. **44**, 757 (1933) are used. Observed I's are from electron impact methods, except those marked with a dagger; these are from Rydberg series limits of spectra by W. C. Price (Phys. Rev. **47**, 419, 510 (1935) and Bull. Am. Phys. Soc. **10**, 9 (1935). In the case of halogen compounds, the predicted and observed I's refer to the *lower* ($^2\Pi_{1\frac{1}{2}}$) of the two values corresponding to the states $^2\Pi_{1\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$ of the positive ion (or analogous states in the polyatomic cases). *Added in proof:* the value 12.9±0.2 for HCl is from A. O. Nier and E. E. Hanson, Bull. Am. Phys. Soc. **10**, 10 (1935). The values for C_2H_5X are from W. C. Price, J. Chem. Phys. **3**, 365 (1935).

definite than for bonding or antibonding orbitals, and have a better theoretical foundation. Available data on observed and predicted I's for such orbitals are given in Table I.

Although the data in Table I are few, certain trends are evident. In analyzing these,* one should first note that the I predictions are directly applicable only to cases in which the orbital of the ionized electron is (*a*) perfectly nonbonding and at the same time (*b*) in an environment (charge distribution) the same as for a free atom. More or less departure from these ideal conditions is to be expected in practise. Interactions of the given orbital with those in other atoms may result in bonding or antibonding tendencies and so cause deviations from (*a*), while changes in the force field due to molecule-formation, including the accumulation of net positive or negative charges on atoms, may cause deviations from (*b*). Besides deviations from (*a*) and (*b*), departures from a "normal" relation, in respect to electron distribution, between the molecule and its positive ion might conceivably be important, but probably are not so in practise. Some discussion bearing on this point will appear in XI of this series.

If we consider the quantities $(I_{pred}-I_{obs})$ from Table I it will be noticed that for each type H_nA or CH_3X, $I_{pred}-I_{obs}$ increases (or becomes decreasingly negative) as we go to more electronegative A or X atoms. (The probable order of increasing electronegativity[6] is H, I, S, C, Br, Cl, N, O.) This effect is just what we might expect, since the accumulation of negative charge on an electronegative atom (e.g. O in H_2O) should make I_{obs} less than I_{pred}.[5] The effect is not observed in the homopolar molecules X_2, where there is no net transfer of charge.

We have, however, not yet accounted for everything. For example, $I_{pred}-I_{obs}=+1.36$ volts for CH_3I, although C and I are nearly equal in electronegativity according to Pauling.[6] Consideration of the fact that the C in CH_3 must bear a considerable net negative charge and the H's a corresponding positive charge solves the difficulty, however. Price has suggested[7] that the resulting field of the CH_3 dipole $H_3{}^+C^-$ accounts partly for the low I_{obs} in CH_3I (and in CH_3Br, CH_3Cl, and other cases). At the same time the C in CH_3 should share its excess negative charge with the I, thus lowering I_{obs} more directly. It is rather artificial to attempt to separate dipole and direct charge accumulation effects, and it is convenient to lump them together under the heading of charge-transfer effects.

While charge-transfer accounts well for $I_{pred}-I_{obs}$ in most cases, it evidently does not suffice for the type HX. In HI, $I_{pred}-I_{obs}=-1.9$ volts, while from charge-transfer one would have expected a small positive value. The observed I's in HCl, HBr, HI may be explained if we assume that, superposed on the normal charge-transfer effect, there is another effect increasing I by about 1.5–2 volts. It is not clear what can be the source of so large an effect, however. Possibilities that occur to one, although they appear quantitatively inadequate, are: united-atom tendency (penetration of H^+ within outer shell of I atom electrons, enough to out-balance effect of the negative electron it brings with it); taking on of some bonding power by $5p\pi_1$, by interaction with the excited orbital $2p\pi$ of hydrogen. It seems hardly worth while to pursue the matter further. Possibly the I_{obs} data, based on electron impact, are seriously in error, although they appear to be unusually

be slightly low because of lack of complete verticality. These doubtful factors, however, are in the aggregate *probably* not of serious importance, and will be tentatively neglected here.

[6] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[7] W. C. Price, Phys. Rev. **47**, 444, 510; J. Chem. Phys. **3**, 256, 365 (1935).

reliable. *Added in proof*: a new electron-impact value for HCl is indeed somewhat lower than the old, while Price (private communication) gets some evidence of Rydberg series leading to lower I's than the old electron-impact values.

In the cases of H_2O, NH_3 and H_2S, it may be noted, the values of $I_{pred}-I_{obs}$ agree very well with what one might expect on the basis of charge-transfer. There is no indication of effects like those in HX, although the possible causes suggested above for the behavior of HX should still operate.

We have not yet considered (except for HX) the possibility that some of the $I_{pred}-I_{obs}$ deviations may be a result of departure from the ideal nonbonding condition, due to interaction with other orbitals. Such interactions must of necessity exist; it is a question here of their importance. The effect should be greatest in cases like Cl_2, where a group $(3p\pi)^4$ is present in each atom. Resonance between the two localized $3p\pi$ atomic types tends to replace them by two new molecular types, one bonding $(\pi+\pi,\ \pi_u)$ and one antibonding $(\pi-\pi,\ \pi_g)$.[5] The latter should have the smaller I, which should therefore correspond to I_{obs}; and if the resonance effect is strong, I_{obs} might for this reason be considerably smaller than I_{pred}. The values of I_{obs} for Cl_2, Br_2 and I_2, although probably not very reliable, tend to indicate that this resonance effect is small, hence that the use of the nonbonding atomic orbitals is a good approximation.

Similar interactions, but smaller because of lack of exact resonance, are to be expected e.g. between the two nonbonding types $3p\pi_{Cl}$ and $5p\pi_I$ in ICl[5] and between the CH_3 radical type $[\pi e]$ and the I atom type $5p\pi_I e$ in CH_3I.[3] In the case of each interacting pair, $5p\pi_I$ has the smaller I. Interaction would tend to give a bonding orbital $(a\pi_{Cl}+b\pi_I)$ or $(a[\pi]_{CH_3}+b\pi_I)$ and an antibonding orbital $(a'\pi_I-b'\pi_{Cl})$ or $(a'\pi_I-b'[\pi]_{CH_3})$, where $a>b$, $a'>b'$, I being increased for the bonding, decreased for the antibonding orbital. For $a=1$, $b=0$, we have the ideal nonbonding case. Since the $I_{min}=I_{obs}$ of ICl and CH_3I is attributed to $5p\pi_I$, any interaction should tend to decrease I_{obs}. I data are lacking for ICl, but for CH_3I (and CH_3X) we might be inclined to attribute the negative values of $I_{obs}-I_{pred}$ (of Table I) largely to such interactions, rather than just to charge-transfer.

Fortunately, there is definite evidence whereby these questions can be settled. The answer is that the interactions are not strong. To begin with, the evidence of the I data on X_2, cited above, should be recalled. Further evidence is found in the fact that the ultraviolet spectra,[5] Rydberg series in particular,[7, 8] involving excitation of one of the nonbonding electrons, show very little vibrational structure. This means that the bonding is little affected by high excitation or removal of the electron in question. This could hardly be true if strong interactions existed between the assumed nonbonding groups of electrons, since the latter would then be replaced by strongly bonding and antibonding groups.

Finally, the intervals $\Delta\nu(^2\Pi_{\frac{1}{2}}-{}^2\Pi_{1\frac{1}{2}})$ observed in the spectra of ICl, IBr, BrCl, and of CH_3Br and CH_3I,[5] and particularly the $\Delta\nu$'s of CH_3I^+, CH_3Br^+, and CH_3Cl^+ obtained from Rydberg series by Price,[8] give rather conclusive independent evidence that the interactions mentioned must be small (i.e., b, b' small) in these molecules, so that they may reasonably be neglected.

The evidence from the $\Delta\nu$'s is as follows. Taking ICl as an example, if one had $(a'\pi_I-b'\pi_{Cl})$ with a' and b' nearly equal, the observed $\Delta\nu$ should be about half-way between those of the Cl and I atoms. Similarly in CH_3I, it should be half-way between $\Delta\nu$ of CH_3 (about zero) and $\Delta\nu$ of I. If, however, $a'=1$, $b'=0$, $\Delta\nu$ should agree approximately with that of the I atom.[9, 3] In all cases the observed $\Delta\nu$'s are found to be in harmony with $a'=1$. Strictly speaking, however, the predicted $\Delta\nu$ should be somewhat increased or decreased according as the I atom has a net positive or negative charge,[9] e.g., $\Delta\nu$ for I should be about 0.69 volt on the basis of I^+, 0.625 volt on the basis of neutral I; observed in CH_3I^+ is 0.62 volt. Presumably the net charge is strongly positive in the excited or ionized states for which the $\Delta\nu$'s are observed. Hence the $\Delta\nu$'s tend to indicate that a' is not quite 1, but nevertheless that $a'=1$, $b'=0$ is much more nearly right than $a'=b'$.

[8] W. C. Price, Phys. Rev. **47**, 419, 510 (1935).
[9] Ref. 5, p. 559.

Summarizing, we conclude that the deviations $I_{pred}-I_{obs}$ for nonbonding atomic orbitals are mainly due to charge-transfer (except in HX?), and that the use of such localized nonbonding atomic orbitals gives good approximations; also that intraradical-bonding orbitals such as $[\pi e]$ of CH_3 may safely be considered as localized, i.e., treated as radical orbitals which are nonbonding so far as interactions with other orbitals are concerned. This last conclusion is in harmony with other evidence in regard to relations between parent molecules and their derivatives.[4]

II. Bonding and Antibonding Orbitals

It is obvious that charge-transfer effects should be important not only for the I's of nonbonding orbitals, but also for those of bonding and antibonding orbitals. Price[7] has already emphasized the importance of dipole effects in this connection. The semi-empirical rules previously set up[5] may be stated as follows:

$$I_{pred} \gtrless \tfrac{1}{2}(I_A^\circ + I_B^\circ), \qquad (1)$$

where the upper inequality sign refers to bonding, the lower to antibonding orbitals, and the I°'s are calculated as earlier indicated.[5] A and B refer to the two atoms forming the bond; if the orbital is a nonlocalized one involving several atoms, the necessary generalization of (1) is easily made. If atoms A and B have effective net charges, the I°'s and I_{pred} must be altered accordingly, but probably not more than 1 or 2 volts in most cases for neutral molecules. Just how large such corrections should be may perhaps best be determined by experience. The same applies to the magnitude of the inequalities indicated by (1); in practice these appear usually to be of the order of 1–3 volts.

For a heteropolar bond involving the usual electron-pair (i.e., excluding the case of one-electron bonds), the charge-transfer effect will generally tend to make I_A° and I_B° more nearly equal than they are for the free atoms. This is because the more electronegative atom usually has the larger I°, which should then usually be decreased by charge-transfer, while the smaller I°, belonging to the more electropositive atom, is at the same time increased. For a homopolar bond, I_A° and I_B° will both be increased or decreased together by charge-transfer, if any. Here the transfer is to or from A and B, from or to other atoms in the molecule. (Example: C−C bonding orbital in C_2H_6, where I°'s should be decreased due to $H_3{}^+C^-$ polarities. This may be expressed, following Price,[7] by saying that I should be decreased by the effects of the two $C^-H_3{}^+$ dipoles.)

In XI of this series it will be shown that the use of molecular orbitals logically implies a comparison not with I°'s of atoms which (at least for the average of A and B) are neutral, but with much smaller I°'s, call them N°'s, corresponding to a condition (cf. Hund) about half-way between neutral atom and negative ion. Instead of (1), this would yield the condition $I_{pred} \gg \tfrac{1}{2}(N_A^\circ + N_B^\circ)$ for bonding and perhaps $I_{pred} > \tfrac{1}{2}(N_A^\circ + N_B^\circ)$ for antibonding orbitals. Such relations, however, are probably unfruitful, since the N's are not accurately known and the magnitudes of the inequalities are large. In practice, the as yet essentially empirical relations (1) promise to be much more useful, since experience so far has shown them reliable.

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Electronic Structures of Polyatomic Molecules. IX. Methane, Ethane, Ethylene, Acetylene

Robert S. Mulliken, *Ryerson Physical Laboratory, University of Chicago*

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Electron configurations for the normal states of C_2H_6, C_2H_4, and C_2H_2 are given, and are used in interpreting observed ionization potentials. Excited orbitals of CH_4 and the others are also discussed and tentative interpretations given for the ultraviolet spectra. "Reduced" interatomic distances are studied as a measure of overlapping and resonance of orbitals of different atoms or radicals.

I. Methane

THE CH_4 problem has already been considered in previous papers[1] but some additional points, especially in regard to excited states, will be taken up here, mainly for the sake of comparisons with ethane and other molecules. The normal and probable lowest excited states of CH_4 (symmetry T_d) are

$$\begin{array}{rl} & 1s^2[sa_1]^2[pt_2]^6,\ {}^1A_1 \text{ and } [pt_2]^{-1}(3sa_1),\ {}^{1,3}T_2 \\ I_{vert}= & 22_{est}\ 14.4_{obs}. \end{array} \quad (1)$$

The symbol $[p]^{-1}(3s)$ means that one $[p]$ electron has been abstracted from the *normal* configuration, and one $(3s)$ has been added; i.e., it means $1s^2[sa_1]^2[pt_2]^5(3sa_1)$.

It is of interest first to compare the observed I (14.4 volts) with that predicted by the usual rules.[2] According to these, we expect

$$I([pt_2]) > \tfrac{1}{2}\{I^\circ(1s_H)+I^\circ(2p_C)\}. \quad (2)$$

By methods given previously,[3] $I^\circ(2p_C)=11.21$ volts, while $I^\circ(1s_H)=13.53$ volts, so that we predict $I([pt_2])>12.37$. Thus the inequality sign here corresponds to about 2 volts, a reasonable value (cf. the case of H_2, where with a bond of comparable or somewhat greater strength, the inequality amounts to 2.4 volts). Proceeding in a similar manner, we may estimate I for $[s]$ of CH_4 as roughly about 22 volts, as given under (1). No experimental value to check this is available.

As lowest excited orbitals of CH_4, it seems reasonable to expect Rydberg, i.e., large atom-like, orbitals $3s$, $3p$, $3d$, etc., with $3s$ lowest. In previous papers,[1] certain LCAO approximate forms[4] were given for CH_4 orbitals, namely, C–H bonding forms corresponding to $[sa_1]$ and $[pt_2]$ of (1), and certain complementary forms called $[s^*a_1]$ and $[p^*t_2]$, similar to $[s]$ and $[p]$, respectively, but of consistently C–H antibonding instead of C–H bonding character. Examination of the nodal surfaces of the LCAO forms $[s^*]$ and $[p^*]$ shows that they are qualitatively very similar to those of $3s$ and $3p$ of an atom. It seems altogether probable, therefore, that $[s^*]$ and $[p^*]$ should be identified with Rydberg orbitals $3s$ and $3p$; and also probable that in this case the *real* molecular orbitals can be much better approximated by suitable $3s$ and $3p$ atomic orbitals, i.e., penetrating central-field orbitals, than by LCAO forms.

An analogous case is that of $(1s-1s,\ \sigma_u)$,—in LCAO symbolism,—of H_2, which in its form, for small r, closely resembles $2p\sigma_u$ of an atom, and does in fact go over into $2p\sigma_u$ of the united-atom as $r\to 0$, and is in fact legitimately considered as $2p\sigma_u$ in the listing of the He-atom-like Rydberg-series-forming excited orbitals of the H_2 molecule.[5]

The selection rules of symmetry T_d allow transitions from the normal state ${}^1A_1$ to the excited state ${}^1T_2$ of (1), also very much weaker transitions to the ${}^3T_2$. The transition ${}^1A_1\to{}^1T_2$ should be strong, since the one-electron jump $[pt_2]\to 3sa_1$ involved is similar to $2p\to 3s$ of an atom: in form $[pt_2]$ strongly resembles $2p$ of an atom.[1] We may then reasonably identify the first intensity maximum (λ about 1250) of the continuous CH_4 absorption[6] with the vertical excitation energy of the transition ${}^1A_1\to{}^1T_2$ ($[p]\to 3s$); we thus get 9.9 volts for that energy. Subtracting this from the observed I (electron-impact, adiabatic?), we get 4.5 volts for the term value of $3s$ in ${}^1T_2$, a reasonable value. This result may be compared with the values 4.6 and 5.2 volts obtained in a similar way for $3s$ from the ultraviolet spectra of NH_3 and H_2O, respectively.[7] (Cf. also the term values 3.85 and 4.20 volts for $3s$ of the N atom in the ${}^2P$ and ${}^4P$ states of $[N^+({}^3P)\cdot 3s]$ and the values 4.08 and 4.45 volts for $3s$ of the O atom in the ${}^3S$ and ${}^5S$ states of $[O^+({}^4S)\cdot 3s]$.) The continuous or diffuse character of the spectra in CH_4, as in NH_3 and H_2O, is attributed to strong predissociation.

The foregoing might lead one to wonder whether in general all excited orbitals of molecules are atom-like Rydberg orbitals. Many well-known examples in diatomic molecules show definitely, however, that this is not the case.

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[1] R. S. Mulliken, J. Chem. Phys. **1**, 490 (1933): V of this series; see p. 500 for CH_3. Also XII of this series, J. Chem. Phys. 1935, in connection with forms and polarities of orbitals.

[2] R. S. Mulliken, J. Chem. Phys. 514: VIII of this series.

[3] a. R. S. Mulliken, Phys. Rev. **46**, 551 (1934); b. J. Chem. Phys. **2**, 789 (1934).

[4] R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935): VI of this series.

[5] Cf. R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932).

[6] A. B. F. Duncan and J. P. Howe, J. Chem. Phys. **2**, 851 (1934).

[7] R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935): VII of this series.

For comparison of CH_4 with certain derivatives, Eq. (1) may be replaced by formulations assuming the symmetry reduced to C_{3v} by a slight distortion. We have

$$[sa_1]^2[\pi e]^4[\sigma a_1]^2,\ {}^1A_1;\ [\sigma a_1]^{-1}(3sa_1)\ {}^{1,3}A_1 \text{ and } [\pi e]^{-1}(3sa_1),\ {}^{1,3}E. \quad (3)$$

The orbital $[pl_2]$ of (1) splits into $[\pi e]$ and $[\sigma a_1]$ and the excited states ${}^{1,3}T$ split into ${}^{1,3}A_1$ and ${}^{1,3}E$.

II. Ethane

In connection with the following discussion of C_2H_6, C_2H_4 and C_2H_2, it is of some importance to know how the distance r_e between the two C nuclei compares with the sizes of $2s$ and $2p$ orbitals of carbon. The results can best be expressed in terms of the quantity[5] $\xi = r_e/2r_a$, where r_a is an effective radius of the $2s$ or $2p$ orbital. Slater gives empirical rules for evaluating r_a roughly; these assume the same r_a for $2s$ and $2p$.[7a] Table I gives values of r_e and ξ for C_2H_n and for some diatomic molecules with which it is of interest to compare these. The r_e data in Table I, except for C_2H_6 and C_2H_4 (electron diffraction) and F_2 (uncertain estimate), are from band spectra.[7b] Although the r_a values have only a rough meaning, they suffice to show that the two C atoms in each C_2H_n are always more compressed, in terms of ξ, than are the two atoms in the isoelectronic diatomic molecule.

The electron configuration of ethane can perhaps best be approximated by treating it, as nearly as may be, as a derivative of CH_4, just as N_2H_4 and H_2O_2 were treated as derivatives of NH_3 and H_2O in a previous paper.[7] Other derivatives of CH_4, in particular those of the type CH_3X, have been discussed in another paper,[8] to which reference should be made. It is also instructive to compare C_2H_6 with the isoelectronic molecule F_2.

The symmetry of C_2H_6 is either D_{3h} (trigonal prism), D_3, or D_{3d} according to the relative angular orientation of the two CH_3 groups around their common axis of symmetry. Although the energy is a minimum for D_{3d} and a maximum for

Table I. *Molecular dimensions.*

No. Elecs.	Molecules	r_e(A.)	ξ	Molecule	r_e	ξ
18	C_2H_6	1.55	1.2	F_2	1.4?	1.7?
16	C_2H_4	1.32	1.0	O_2	1.20	1.3
14	C_2H_2	1.20	0.9	N_2	1.09	1.0
				Cl_2	1.98	1.3

D_{3h}, the difference is probably so small[8a] that essentially "free rotation" occurs, and the symmetry D_3 characteristic of intermediate rotation angles may be taken as typical. Consideration of D_{3h} and D_{3d} is principally of interest in connection with electronic selection rules, since some transitions which are allowable according to the relatively liberal selection rules of D_3 are forbidden according to those of D_{3h} or of D_{3d} or sometimes of both.* In such cases we are justified in concluding that the transitions in question are weak even for D_3.

If we assume symmetry D_3, the normal state of C_2H_6, omitting carbon $1s$ electrons, may be be described as

$$[sa_1]^2[sa_1]^2[\pi e]^4[\pi e]^4[\sigma+\sigma, a_1]^2,\ {}^1A_1 \quad (4)$$

approx. location $CH_3\ CH_3\ CH_3\ CH_3\ H_3C-CH_3$

est. vert. I two values aver. about 22? | two val. close to 14.5 | 12

All the orbitals used in (4) are CH_3 radical orbitals, except for the C−C bonding orbital $[\sigma+\sigma]$, which may be thought of as built approximately from $[\sigma]$'s of two CH_3 radicals. The electron configuration (4) has a strong similarity to that of a halogen molecule, in particular F_2, for which we have[3a]

$$\underset{F}{(2s)^2}\underset{F}{(2s)^2}\underset{F}{(2p\pi)^4}\underset{F}{(2p\pi)^4}\underset{F-F}{(2p\sigma+2p\sigma,\ \sigma_g)^2},\ {}^1\Sigma_g^+.$$

Resonance between the two $[\pi e]$'s in (4) should of course exist, but is probably weak (see below) and should then give rise to only a small splitting of the I value. It can then be predicted that the latter should not differ much from the value 14.4 volts for $[\pi e]$ in CH_4 (cf. (1), (3) above), since the field of force for $[\pi e]$ here should not be much different than in CH_4 or CH_3X.[8]

[7a] Cf. J. C. Slater and N. H. Frank, *Introduction to Theoretical Physics* (McGraw-Hill & Co., 1933), p. 432.
[7b] Cf. R. de L. Kronig, *The Optical Basis of Chemical Valence* (MacMillan Co., New York, 1935).
[8] R. S. Mulliken, Phys. Rev. **47**, 413 (1935).
[8a] Cf. H. Eyring, J. Am. Chem. Soc. **54**, 3200 (1932). K. Yardley, Proc. Roy. Soc. **A118**, 449 (1928) finds symmetry D_{3d} for C_2Cl_6 (in crystals).
* Cf. reference 11.

The strength of resonance between pairs of orbitals like the foregoing $[\pi e]$ or the two $[sa_1]$ in (4) can be gauged somewhat by the ξ values in Table I, as compared to what is known for molecules like N_2 and O_2. We know that in N_2, resonance between π orbitals of the two atoms is strong, giving $(\pi+\pi)$ and $(\pi-\pi)$. The same is true in O_2, but probably not in F_2 or other halogens.[2] Although ξ for C_2H_6 is less than for O_2, this is not a fair indication of the degree of overlapping of the $[\pi e]$'s of the two CH_3. Since the $[\pi e]$'s give strong C−H bonding in each radical, they are doubtless concentrated largely between the H_3 plane and a parallel plane through the carbon nucleus, but with centers of gravity somewhat nearer the H_3 plane; in size and form they perhaps resemble $2p\pi$ orbitals of an N or O atom (cf. discussion of $[p\pi]$ orbitals of CH_4 in *V* of this series, section 11 and Eqs. (6); also in XII of this series). The height of the CH_3 pyramid, assuming tetrahedral valence angles, is $\frac{1}{3}$ of the C−H distance, i.e., about $\frac{1}{3}$ of 1.1A, or 0.36A. Thus the center of gravity of each $[\pi e]$ is about 0.2A from the C atom, so that the mean distance apart of $[\pi e]$ orbitals of the two CH_3 radicals is about 0.4A greater than the C−C distance, or about 1.95A. This gives for them an effective ξ of 1.5 if we use r_a of the C atom, or somewhat more if a more suitable effective ξ is used. Thus the degree of overlapping of the $[\pi e]$'s in C_2H_6 is clearly much smaller than that of the π's in O_2, probably comparable with that of the π's in F_2, so that resonance between them should be small. This justifies our use of radical orbitals $[\pi]$ rather than whole-molecule orbitals $[\pi+\pi]$ and $[\pi-\pi]$.

In the case of N_2 we know, from the value of an *I* which must be attributed to $(s-s)$, that there is very strong resonance between the atomic 2*s* orbitals, so that the use of $(s+s)^2(s-s)^2$ gives a better approximation[3a] than the use of $2s^22s^2$. For 2*s* of O, there is no direct evidence from band spectra or *I*'s, yet it is hard to believe that there is not strong resonance between the 2*s*'s in view of the existence of strong resonance for the $2p\pi$'s, for which the overlapping is less favorable than for the 2*s*'s. (It should be noted that, for a given ξ, strong overlapping sets in at smaller *r* values for $p\pi$'s than for $p\sigma$'s or *s*'s. Really, it would be more logical to give a separate ξ for the π orbitals, using the same r_e but smaller r_a.)

Resonance between the $[sa_1]$ orbitals of the two CH_3 in C_2H_6 is probably fairly strong (unlike the case of F_2), since ξ has a value between those of N_2 and O_2 and since in CH_4 the orbital $[sa_1]$ is not restricted to a CH_3 group but also helps hold the fourth H, which is here replaced by a second CH_3 group. For strong resonance one should write

$$[s+s, a_1]^2[s-s, a_2]^2[\pi e]^4[\pi e]^4 [\sigma+\sigma, a_1]^2, {}^1A_1. \quad (4a)$$

Here *I* should be considerably greater for $[s+s]$ than for $[s-s]$. The orbitals $[s\pm s]$ in LCAO approximation are constructed as linear combinations of $[s]$ orbitals of the two CH_3 and so, like the latter, involve considerable C−H bonding.

At the same time, one has to admit some interaction between $[s+s]$ and $[\sigma+\sigma]$, giving two new partially mixed forms; such hybridization should increase *I* for $[s+s]$ and decrease it for $[\sigma+\sigma]$. It is difficult to estimate the extent of this mixing effect, but the writer is inclined on the whole to think that it is not large.

The C−C bonding orbital $[\sigma+\sigma]$ must be admitted to give a little bonding between each C and its 3H, as one sees by comparison with the related orbital $[\sigma a_1]$ of CH_4. Hence $[\sigma+\sigma]$ is not quite completely localized in the C−C bond. If, however, we neglect this and also neglect mixing with $[s+s]$, $[\sigma+\sigma]$ may be represented roughly by

$$a(2p\sigma+2p\sigma),$$

and has approximately the symmetry σ_g of the bonding orbital $(\sigma+\sigma)$ of a diatomic molecule like F_2. Following the usual rule,[2] we may predict that

$$I_{vert}(\sigma+\sigma) > I^\circ(2p\sigma_C).$$

By methods given previously,[3] one obtains $I^\circ = 11.21$ volts for $2p\sigma_C$, hence one predicts $I(\sigma+\sigma) > 11.21$ volts. Since the C−C bond in C_2H_6 is strong, one might expect the inequality sign to represent perhaps about 2 volts as in typical cases with strong bonds. In accordance with a point made by Price,[9] to the effect that *I* of the C−C bonding electron must be reduced by the fields of the two CH_3 dipoles (polarity $H_3{}^+C^-$), it seems likely that above-estimated I° should be reduced by as much as 1 or 2 volts. The

[9] W. C. Price, Phys. Rev. **47**, 444 (1935): C_2H_2, C_2H, C_2H_6.

net result is a predicted value of about 11 or 12 volts for the vertical I of $(\sigma+\sigma)$. The adiabatic I should be considerably less, since the C−C bonding should be markedly loosened by removal of one of the two $[\sigma+\sigma]$ electrons.

Another mode of approach is to consider the formation of C_2H_6 from two CH_3. The structure of CH_3 is given by

$$[sa_1]^2[\pi e]^4[\sigma a_1],\ ^2A_1,$$

and I_{vert} for $[\sigma a_1]$ is believed to be about 8.5 or 9 volts, both for free CH_3 (which may be plane) and for CH_3 constrained to the shape it has within C_2H_6.[1] Now $[\sigma+\sigma, a_1]$ of C_2H_6 and $[\sigma a_1]$ of CH_3 are related in the same way as, e.g., $(\sigma+\sigma, \sigma_g)$ of F_2 and $2p\sigma$ of F. Hence we might expect

$$I_{vert}([\sigma+\sigma]) > I^\circ_{vert}([\sigma a_1]).$$

Here I°_{vert} is just I_{vert} of $[\sigma a_1]$ of CH_3. If we assume 2.5–3 volts for the inequality sign, I_{vert} $([\sigma+\sigma])$ comes out again with a predicted value of 11–12 volts.

Experimentally, we have only Morris' electron-impact value[10] of 12.8 volts for I of C_2H_6. Since Morris' values for C_2H_4 and C_2H_2 were, respectively, 12.2 and 12.3 volts, as compared with the values 10.41 and 11.35 determined later by spectroscopic methods,[9] we may apply a correction of about −1.4 volts to Morris' value, giving as a probable corrected experimental value 11.4 volts. This, however, would be an adiabatic value, and the true vertical value might then be about 12.4 volts, which is in reasonable agreement with our estimates. At any rate, there seems to be little doubt that the minimum I of C_2H_6, whether measured vertically or adiabatically, must belong to $[\sigma+\sigma]$.

Turning now to excited orbitals and states of C_2H_6, it appears likely that the lowest excited orbital is of essentially $3s$ type. In analogy to our previous discussions[7] of N_2H_4 and H_2O_2, we might first think of a $3s$ orbital for each CH_3 radical. Since these overlap strongly, however, we should then form linear combinations $a(3s\pm3s)$, of which the form $a(3s+3s)$ must have the lower energy. It is readily seen that this form is rather closely similar to that of a single $3s$ function centered about the mid-point of the C−C line. The lowest excited states may well be those obtained by exciting one $[\sigma+\sigma, a_1]$ electron of (4) and putting it into $3sa_1$, giving

$$[\sigma+\sigma, a_1]^{-1}(3sa_1),\ ^{3,\ 1}A_1. \qquad (5)$$

On examining the electronic selection rules for symmetry D_3, however, we find that transitions from A_1 to A_1 are forbidden,[11] so that (4)→(5) should not occur. [Weak violations of this prohibition may nevertheless occur because of coupling between electronic and vibrational motions.[11a]]

What, then, are the lowest excited states to which transitions are not forbidden? If one of the $[\pi e]$ electrons of (4) is excited to $3sa_1$, the result is

$$[\pi e]^{-1}(3sa_1),\ ^{1,\ 3}E,\ ^{1,\ 3}E. \qquad (6)$$

Transitions from $^1A_1$ to ^1E (and weakly to ^3E) are allowed, and one of these should in fact probably be strong, the electron transition being essentially $[\pi e]\rightarrow 3s$ within either CH_3 radical, resembling $2p(\pi)\rightarrow 3s$ of an atom.

There are two ^1E and two ^3E in (6) because of resonance between the configurations $[\pi]^4[\pi]^3$ and $[\pi]^3[\pi]^4$ which are implied by $[\pi]^{-1}$. This resonance corresponds to an incipient tendency toward two conditions which we could express in LCAO symbols[4] by writing $[\pi+\pi, e]^4[\pi-\pi, e]^3$ and $[\pi+\pi, e]^3[\pi-\pi, e]^4$. Recognizing that $3sa_1$ here is of the LCAO type $(3s+3s, a_1)$, one finds that the only strong transition is the $^1A\rightarrow{}^1E$ involving the ^1E state of type $[\pi+\pi]^3[\pi-\pi]^4$, the higher-energy one of the two. This follows if we note that for symmetry D_{3d}, state (4) is $^1A_{1g}$ while (6) becomes $^{1,\ 3}E_g$ (lower), $^{1,\ 3}E_u$ (higher), the latter involving $[\pi+\pi, e_u]^3[\pi-\pi, e_g]^4(3s+3s, a_{1g})$; only $g\rightarrow u$ transitions are allowed for symmetry D_{3d}.

We are now in a position to understand the observed close similarity[10, 12] of general appearance between the ultraviolet spectra of CH_4 and C_2H_6. In both cases the spectrum is continuous with indications of only a few diffuse bands. Very faint absorption begins near λ1800, at least in CH_4 (1 atmos. pressure, 15 mm path). The intensity increases steadily as λ decreases, reaching a maximum in CH_4 near λ1250, and in C_2H_6 near λ1350, so far as can be judged by the published descriptions.[6, 9] This close similarity is just what we should expect assuming that in both cases we have an excitation process $[\pi e]\rightarrow 3s$, with nearly the same energy relations in both

[10] J. C. Morris, Phys. Rev. **32**, 456 (1928).

[11] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

[11a] Cf. G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

[12] G. Scheibe and H. Grieneisen, Zeits. f. physik. Chemie **B25**, 52 (1934).

cases. As we have seen, I is expected to be about the same for $[\pi e]$ in C_2H_6 as in CH_4, while the term value of $3s$ may well also be nearly the same in both.

Of course in CH_4, $[\pi e]\rightarrow 3s$ is accompanied by and coincident with $[\sigma a_1]\rightarrow 3s$, since $[\pi e]$ and $[\sigma a_1]$ of symmetry C_{3v} together make $[pt_2]$ for symmetry T_d (cf. (1) and (3)). In C_2H_6, however, the transition $[\sigma+\sigma]\rightarrow 3s$, although it rather corresponds to $[\sigma a_1]\rightarrow 3s$ of CH_4, would come at much longer wavelengths (absorption maximum perhaps near λ1600),—see above. If this transition were not forbidden in C_2H_6, the similarity in wavelength distribution between the CH_4 and C_2H_6 spectra would not occur.

Before the matter of C_2H_6 excited states is dismissed, the C−C antibonding excited orbital $[\sigma-\sigma, a_2]$ should be mentioned (cf. discussion of analogous orbitals in H_2O_2 and N_2H_4).[7] Examination of the form of this shows that its nodal surfaces resemble those of the atomic orbital $3p\sigma$ and it seems likely that $[\sigma-\sigma]$ plays this role in C_2H_6.

Cf. the C−H antibonding orbitals $[s^*]$ and $[p^*]$ in CH_4 (obtained by LCAO methods), which apparently function as, or are replaced by, $3s$ and $3p$. In C_2H_6, as we have seen, our $3s(C_2H_6)$ corresponds to an LCAO form $[3s(CH_3)+3s(CH_3)]$, while $3s(CH_3)$ in turn corresponds to an LCAO C−H antibonding form $[s^*]$ similar to that of CH_4. Similarly $3p\pi(C_2H_6)$ may be identified with the LCAO form

$$[3p\pi(CH_3)+3p\pi(CH_3)]\approx\{[\pi^*](CH_3)+[\pi^*](CH_3)\}.$$

The writer is inclined to think that the excited states derivable by exciting a $[\sigma+\sigma]$ electron to $[\sigma-\sigma]$ are higher than those of either (5) or (6), or at least than those of (5). Reasons for this opinion will be given in a later paper dealing more systematically with excited orbitals.

III. Ethylene

Ethylene has already been discussed in previous papers.[11, 13, 12a] In its normal state (symmetry V_h), the electron configuration, omitting carbon $1s$, can perhaps best be represented by

$$[s+s, a_{1g}]^2[s-s, b_{1u}]^2[yb_2]^2[yb_2]^2[\sigma+\sigma, a_{1g}]^2[x+x, b_{3u}]^2,\ {}^1A_{1g} \qquad (7)$$

locn.	$H_2C-CH_2H_2C\leftrightarrow CH_2$	CH_2	CH_2	H_2C-CH_2	C−C
est. I_{vert}		about 14.5	12 or 13?		11

Here $[\sigma+\sigma]$ might just as well be called $[z+z]$, but we shall use $[\sigma+\sigma]$ because it is used for a corresponding orbital in C_2H_6, C_2H_2 and other cases. The axes z, y, x are, respectively, along the C−C axis, in the plane of the molecule perpendicular to this axis, and perpendicular to the plane of the molecule. The representation symbol b_2 belonging to the CH_2 radical orbitals in (7), belongs to the local symmetry (C_{2v}) of these radicals. The other representation symbols a_{1g}, b_{1u}, b_{3u} in (7) belong to the symmetry V_h of the molecule-as-a-whole.

Attention should perhaps be called to the meaning and implications of the orbital symbols in (7). The symbol $[s+s]$ means a certain whole-molecule orbital which could be *approximately* built by taking $a\{[s]_A+[s]_B\}$, where $[s]$ refers to an orbital of one of the CH_2 radicals. The symbol $[s]$ in turn represents an orbital which could be built in LCAO *approximation* from a linear combination of $2s$ of carbon and $1s$ of two H atoms (cf. IV of this series). Since $[s]$ involves C−H bonding, so does $[s+s]$, but $[s+s]$ also involves C−C bonding. The estimated relative importance of C−H and C−C bonding for the various orbitals is indicated under the electron configuration in (7). It will be noted that $[s+s]$, $[s-s]$, and $[\sigma+\sigma]$ are inter-radical orbitals of completely nonlocalized type.

The orbitals $[y]$ are localized to the extent of being each restricted to one CH_2 radical, although not localized within the latter. The symbol $[x+x]$ describes an orbital which can be constructed in LCAO approximation as $a\{(2p_x)_A+(2p_x)_B\}$, where each $2p_x$ is a CH_2 radical orbital which happens to be of particularly simple type, being, namely, just a nonbonding C atom orbital. Because each $2p_x$ is localized on the C atom of CH_2, $[x+x]$ is partially localized in C_2H_4, being confined to the C−C bond. It is an inter-radical orbital, but of semi-localized type.

[12a] C. P. Snow and Alsopp, Trans. Faraday Soc. **40**, 93 (1934) have recently made a careful study of the ultraviolet spectra of C_2H_4 and some of its derivatives.

This supports (9) as upper level of the C_2H_4 bands. This paper was unfortunately overlooked until the present paper was in proof.

[13] a. R. S. Mulliken, Phys. Rev. **41**, 751 (1932). b. Also W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934); Proc. Phys. Soc. London **46**, 333 (1934): C_2H_4 and C_2H_6.

The electron configuration (7) of C_2H_4 has relations[13a] to that of the isoelectronic molecule O_2, but they are much less close than those between the configurations of C_2H_6 and F_2, or of C_2H_2 and N_2. This is because the change of symmetry from C_2H_4 to O_2 is much more radical than from C_2H_6 to F_2, or C_2H_2 to N_2 (no change at all in the latter).

If (7) is used for C_2H_4, we must admit the existence of resonance and a double I for the two $[y]$ orbitals. This resonance must be stronger than that of the two $[\pi]$'s in C_2H_6 or the two π's in F_2, but is probably still not very strong. An effective ξ can be estimated in the same way here for the $[y]$'s of the two CH_2 as was done above for the $[\pi]$'s of the two CH_3 in C_2H_6. Assuming an H−C−H angle of 120°, the center of gravity of each $[y]$ orbital is about 0.3A from the C atom, and the mean distance between the two $[y]$'s is about 1.9A. This makes the effective ξ nearly as great as for the $[\pi]$'s in C_2H_6, and much greater than for the $2p_x$'s which are used to form $[x+x]$ here, since the latter involve no C−H bonding and are centered at the carbon atoms.

There must be more or less mixing between the pure LCAO forms $[s+s, a_{1g}]$ and $[\sigma+\sigma, a_{1g}]$ and again between $[s-s, b_{1u}]$ and $[\sigma-\sigma, b_{1u}]$, the last an excited type not present in (7). The mixing is probably stronger than for the analogous C_2H_6 orbitals, in view of the smaller ξ (cf. Table I) and the stronger C−C bond. It is difficult to devise a simple yet descriptive LCAO symbolism to indicate such mixing. If we had complete, i.e., 50–50, mixing, it would be best to replace the symbols $[s\pm s]$ and $[\sigma\pm\sigma]$ by new symbols such as $[q^+\pm q^+]$ and $[q^-\pm q^-]$. If for the moment we neglect the participation of hydrogen 1s functions in $[s]$ and $[\sigma]$, then the q's represent 50–50 mixtures of carbon 2s and 2$p\sigma$, of the same sort that occur in the linear Stark effect of the H atom for $n=2$. (These q's have been used by Pauling under the designations σ_b, σ_0 in discussing the structure of N_2.) We should then have

$$q^+ = 2^{-\frac{1}{2}}(2s+2p\sigma), \quad q^- = 2^{-\frac{1}{2}}(2s-2p\sigma),$$

where the signs are to be so understood that each q^+ is strong in the direction of the other C atom, q^- in the direction of the neighboring H atoms. Instead of the q's just given, corresponding $[q]$'s in which hydrogen 1s functions participate must of course be used in constructing the forms $[q\pm q]$ which we are considering.

For the ideal case of 50–50 $s-p\sigma$ mixing, (7) would be replaced by

$$[q^+ + q^+, a_{1g}]^2[q^- - q^-, b_{1u}]^2[q^- + q^-, a_{1g}]^2 \times [yb_2]^2[yb_2]^2[x+x, b_{3u}]^2, \ {}^1A_{1g}. \quad (7a)$$

The actual case must be intermediate between (7a) and that which is represented by (7) if in the latter the symbols $[s\pm s]$ and $[\sigma+\sigma]$ are taken to represent pure LCAO forms without any $s-p\sigma$ mixing. For the sake of simplicity, however, we shall in practice *let the symbolism in* (7) *represent the intermediate case* just described. That is, we shall in practise use $[s+s]$ to represent something between the pure $[s+s]$ and $[q^+ + q^+]$, $[s-s]$ something between pure $[s-s]$ and $[q^- - q^-]$, $[\sigma+\sigma]$ something between pure $[\sigma+\sigma]$ and $[q^- - q^-]$. This is not unreasonable, since our practical $[s+s]$ is always (by definition) nearer to the pure $[s+s]$ than to the pure $[\sigma+\sigma]$, and so on. It might be contended that it would be better to use the symbols $[q^+ + q^+]$ etc. appropriate to 50–50 mixing whenever these represent better approximations than pure forms $[s+s]$ etc. That is, for mixtures in the range between 75, 25 and 25, 75 proportions, we might use the $[q\pm q]$ symbols, reserving $[s\pm s]$ and $[\sigma\pm\sigma]$, respectively, for mixtures between 0, 100 and 25, 75, and between 75, 25 and 100, 0. The difficulty is that in practise we usually are not yet sure whether or not the actual proportions in a given case come within the 75, 25 to 25, 75 range; and furthermore, our symbolism would suffer unnecessary complication in trying to make the distinction.

With the foregoing understanding as to symbolism we return to (7) to note that the distribution of C−H and C−C bonding power among the practical orbitals $[s+s]$, $[s-s]$, and $[\sigma+\sigma]$ varies according to the degree of $s-p\sigma$ mixing. The forms of *pure* $[s+s]$, $[s-s]$, and $[\sigma+\sigma]$ are such that pure $[s+s]$ is (probably strongly) C−C bonding and at the same time (probably weakly) C−H_2 bonding; $[s-s]$ is C−C antibonding (C⟷C) but may be strongly C−H_2 bonding; $[\sigma+\sigma]$ is mainly C−C bonding but has some C−H_2 bonding power. Hybridization

between $[s+s]$ and $[\sigma+\sigma]$ should alter their relative C−C and H_2−C bonding powers, probably increasing the C−C and decreasing the C−H_2 for $[s+s]$ with the reverse effect for $[\sigma+\sigma]$.

Understanding of the structure of C_2H_4 is helped by considering its formation from 2 CH_2.[13a, 11] To get (7) with *pure* $[s+s]$ etc., two excited CH_2 radicals are needed, each in the condition

$$[sa_1]^2[yb_2]^2[za_1](2p_xb_1),\ ^{1,\,3}B_1. \qquad (8)$$

To get (7*a*), we should need two CH_2 radicals in an artifically constructed excited condition

$$[q^-a_1]^2[q^+a_1][yb_2]^2[2p_xb_1],\ ^{1,\,3}B_1. \qquad (8a)$$

For the actual (7), with impure $[s+s]$ etc., something between (8) and (8*a*) is needed; or, practically, the symbols $[sa_1]$ and $[za_1]$ in (8) may be understood to be mutually contaminated forms.

Lennard-Jones[14] has described the process of putting a radical (e.g., here CH_2) into an artificially constructed state, suited to the condition of the radical when combined, as "reorganization." The proper reorganized state to be used comes under the heading of "valence states,"[3b] a term introduced by Van Vleck. The proper valence state here has not only to be intermediate between pure (8) and (8*a*), but also between the $^1B_1$ and $^3B_1$ condition, although nearer the latter (cf. discussions of the valence states of atoms[3b]). As a result of the reorganization of the normal state of CH_2 to get the proper valence state, there is some readjustment of the relative C−H bonding powers of $[sa_1]$ and $[za_1]$ as compared with normal CH_2.

Prediction of I's is rather difficult for C_2H_4. The CH_2 orbital $[yb_2]$ is essentially the same as the $[y]$ component[1] of the degenerate orbital $[\pi e]$ of CH_3 in C_2H_6, CH_3X, or CH_4 and, although the charge distribution in its environment is considerably different here than in those cases, it still seems probable that I is about the same as there, i.e., about 14.5 volts. For $[\sigma+\sigma]$ the predicted I depends on how strong the hybridization is with $[s+s]$. For zero hybridization, the predicted value would be about 12 volts as in C_2H_6. Hybridization would presumably tend to diminish this, yet increased C−H bonding would apparently tend the other way, by partly removing $[\sigma+\sigma]$ from between the negatively charged C atoms. For $[x+x]$ we predict $I>I^\circ(2p_x)_C$, i.e., $I>11.2$ volts,[3] subject to correction for charge-transfer effects (polarities $H_2{}^+C^-C^-H_2{}^+$). Roughly estimating the charge-transfer correction on I° as −1.5 and the magnitude of the inequality sign as +1.5 volts, we arrive at about 11 volts for the estimated vertical I of $[x+x]$.

For the experimental I_{min} of C_2H_4 the best value is probably 10.41 volts, obtained by Price from a Rydberg series in the ultraviolet absorption spectrum.[9] This is of course an adiabatic I, and the vertical I must be greater, since from (7) the electron removed can hardly help being a bonding electron. The vertical I might then be about 10.7 or possibly 11 volts, which agrees with the predicted value for $[x+x]$.

The possibility that the observed I belongs to $[\sigma+\sigma]$ rather than $[x+x]$, or that both have nearly the same value, cannot, however, be definitely excluded, since our predictions have a considerable margin of uncertainty. The relatively moderate amount of vibration accompanying Price's Rydberg series bands tends to indicate that the observed I is nearly vertical. This is rather surprising in view of the fact that a bonding electron ($[x+x]$ or $[\sigma+\sigma]$) is removed. Possibly it might be explained if it is the $[\sigma+\sigma]$ which is removed, and if this is only weakly C−C bonding and at the same time moderately strongly C−H bonding, a situation which is conceivable as a result of hybridization between $[s+s]$ and $[\sigma+\sigma]$. Or if it is the $[x+x]$ which is removed, perhaps the resultant weakening of the bond is less pronounced than one would be inclined to expect.

The longest wavelength absorption of C_2H_4 has been attributed in previous papers[11, 13a] to a transition from (7) to an excited state ^1B_u:

$$[x+x]^{-1}[x-x, b_{2g}],\ ^{3,\,1}B_{1u}, \qquad (9)$$

i.e. to a transition of an electron from $[x+x]$ to $[x-x]$.[12a] It is reasonable to expect that the orbital $[x-x]$ is the lowest excited orbital and that it is far from being of a Rydberg series type; it should resemble the x component of the degenerate orbital $(\pi-\pi, \pi_g)$ which is known in O_2.[13a] Another possible excited orbital is $[\sigma-\sigma, b_{1u}]$, but it is probable that this is very high in

[14] J. H. Lennard-Jones, Trans. Faraday Soc. **30**, 70 (1934).

energy, and it may resemble a $3p\sigma$ Rydberg orbital, as was suggested above for the similar orbital $[\sigma-\sigma]$ of C_2H_6.

Among others, the following excited states of C_2H_4 might be considered (the $^{-1}$ symbols are relative to (7)):

$$\begin{array}{l}[x+x]^{-1}(3sa_{1g}),\ {}^{1,3}B_{3u};\\ [\sigma+\sigma]^{-1}(3sa_{1g}),\ {}^{1,3}A_{1g};\\ [\sigma+\sigma]^{-1}[x-x],\ {}^{1,3}B_{2g};\\ [x+x]^{-1}[\sigma-\sigma],\ {}^{1,3}B_{2g};\\ [\sigma+\sigma]^{-1}[\sigma-\sigma],\ {}^{1,3}B_{1u}.\end{array} \qquad (10)$$

The selection rules, however, forbid transitions from the normal state (7) to any of these except the B_{1u} and B_{3u}. The $[\sigma+\sigma]^{-1}[\sigma-\sigma]$, $^{3,1}B_{1u}$ is probably of high energy, so probably need not be considered here for the longer wavelength spectra. This leaves only $[x+x]^{-1}(3sa_{1g})$, $^{1,3}B_u$ as a possible competitor of (9) as upper level of the longest wavelength observed bands.

It was shown in a previous paper[13a] that the assumption of a transition $[x+x]\rightarrow[x-x]$, i.e., (7)→(9), affords a reasonable explanation of the photochemical transformations *cis*↔*trans* which occur in C_2H_4 derivatives on absorption of ultraviolet light. The alternative possibility $[x+x]\rightarrow 3s$, i.e., (7)→$[x+x]^{-1}(3s)$, $^{1,3}B_u$ of (10), is found on examination not to afford such an explanation. Hence it seems very probable that the ultraviolet absorption which gives rise to *cis*↔*trans* transformations in C_2H_4 derivatives is indeed of the type $[x+x]\rightarrow[x-x]$.

The absorption spectra of the simpler C_2H_4 derivatives[12, 15] show indications of two continuous absorption regions, a weaker one with maximum about λ2150, a stronger one with maximum near λ1800. In the simplest derivatives, the "maximum" near λ2150 appears only as a point of inflection in the absorption curve.[12a]

In C_2H_4 itself[12, 15], the whole absorption is very much weaker. Its appearance indicates, according to Scheibe and Grieneisen,[12] that there are two overlapping systems of bands, the first increasing steadily in intensity from about λ2000 to perhaps about λ1800 ($\nu=55{,}560$), the second starting abruptly with a maximum intensity at $\nu=57{,}320$. These characteristics indicate a considerable change in molecular dimensions in the first system, little change in the second.[12a]

It seems likely that the first absorption region in C_2H_4 and its derivatives may be associated with $[x+x]\rightarrow[x-x]$, the second with $[x+x]\rightarrow 3s$. Assuming $I_{vert}=$ about 11 volts for $[x+x]$, the $3s$ term value comes out about 4 volts, a fairly reasonable value (cf. CH_4), while the $[x-x]$ term value is somewhat greater.

No good reason is evident why the absorption should be so much weaker in C_2H_4 than in its derivatives, since the transitions considered are allowed by the selection rules both for C_2H_4 and the derivatives. Nor is it clear why there should be a displacement toward shorter wavelengths. Much more work will probably be needed before this and similar problems for other molecules will be solved; and it may be that the interpretations given in the present series of papers will need serious modification in the case of excited states.[12a]

In the foregoing it has tacitly been assumed that the orbitals $[x+x]$, $[\sigma+\sigma]$, $[x-x]$, $3s$ are nearly the same, and obey the same selection rules, in C_2H_4 derivatives as for C_2H_4 itself. This is probably true, except for probably weak transitions violating the rather strict selection rules of C_2H_4, since the orbitals mentioned, except perhaps $[\sigma+\sigma]$, are fairly well localized in the neighborhood of the C=C bond. This neighborhood should usually not be very much affected by changes elsewhere in the molecule. The situation is, however, altered seriously in the case of conjugated double bonds or unsaturated rings, which have been discussed by others. Also in the case of C_2H_4 derivatives in which atoms or radicals have been introduced (e.g., I, Br, NH_2) which have nonbonding orbitals of low I, the latter may of course cause new absorption bands to appear in the same region as the $[x+x]\rightarrow[x-x]$ bands or even at longer wavelengths.

IV. Acetylene

The normal state of acetylene (symmetry $D_{\infty d}$ like the isoelectronic molecule N_2) may be described, omitting carbon $1s$, as

[15] J. Stark and collaborators, *Jahrb. der Rad. und Elek.* Vol. 10, 141–188 (1913): C_2H_4, C_2H_2, and derivatives.

$$(s+s,\sigma_g)^2(s-s,\sigma_u)^2(\sigma+\sigma,\sigma_g)^2(\pi+\pi,\pi_u)^4,\ {}^1\Sigma^+_g \qquad (11)$$

	HCCH	HC↔CH	HCCH	C=C
locn.				
est.	15 or 16?	13 or 14?	11.6	
vert. I				

The electron configuration given by (11) is formally identical with that for N_2,[3a] except for a probable reversal of the energy order of $(\sigma+\sigma)$ and $(\pi+\pi)$. The main differences as compared with N_2 are connected with the C−H bonding properties of the σ orbitals. These arise because the latter, in LCAO approximation, are linear combinations, not of pure C atom orbitals $2s$ or $2p\sigma$, but of certain σ orbitals of CH (see below) which already involve C−H bonding, being themselves, in LCAO approximation, combinations of $1s_H$ with C atom orbitals. The $(\pi+\pi)$ orbital, on the other hand, is built from practically pure $2p\pi$ of carbon.

The very close approach of the two CH radicals in C_2H_2 (cf. Table I) should cause a very large difference in I between $(s+s)$ and $(s-s)$. The strong interaction should also bring about marked $s-p\sigma$ hybridization, i.e., strong mixing between $(s+s)$ and $(\sigma+\sigma)$, both of which are σ_g, and again between $(s-s)$ and the (excited) orbital $(\sigma-\sigma)$, both σ_u. This mixing should tend to increase the I of $(s+s)$ and of $(s-s)$, to decrease those of $(\sigma+\sigma)$ and $(\sigma-\sigma)$. Quite possibly the mixing is so strong that it would be a better approximation to write

$$(q^++q^+,\sigma_g)^2(q^--q^-,\sigma_u)^2(q^-+q^-,\sigma_g)^2 \times(\pi+\pi,\pi_u)^4,\ {}^1\Sigma^+_g \qquad (11a)$$

instead of (11). At any rate, something between (11) and (11*a*) should be correct. For the sake of simplicity, we may in practice use (11) to represent this intermediate condition, by letting the symbols $(s+s)$, $(s-s)$, $(\sigma+\sigma)$ imply not pure $(s+s)$ etc. but partially mixed forms, just as we did in the case of the similar symbols for C_2H_4 (cf. discussion following Eq. (7*a*)).

The molecular orbital indicated in LCAO approximation by (q^++q^+) would give very strong C−C bonding and simultaneous weak C−H bonding, (q^--q^-) weak C−C antibonding and strong C−H bonding, (q^-+q^-) weak C−C bonding and strong C−H bonding. The relations for pure $(s+s)$, $(s-s)$, and $(\sigma+\sigma)$ are similar, but differ in the distribution of bonding strengths, particularly in that pure $(s-s)$ should give strong C↔C antibonding.

Light is thrown on the structure of C_2H_2 not only by comparing it with N_2, but also by examining its relationship to CH+CH. The configuration (11) or (11*a*) can be thought of as derived by bringing together two CH radicals each in a suitable "reorganized" valence state (cf. discussion of CH_2+CH_2 following Eq. (8*a*) above). The proper reorganized state for pure (11) would be a certain mixture of the four states

$$1s^22s\sigma^2(1s_H+2p\sigma,\sigma)2p\pi^2,\ {}^4\Sigma^-,\ {}^2\Sigma^+,\ {}^2\Delta,\ {}^2\Sigma^- \qquad (12)$$

For (11*a*) it would be a mixture of the four states

$$1s^2(2q^-\sigma+1s_H,\sigma)^22q^+\sigma2p\pi^2,\ {}^4\Sigma^-,\ {}^2\Sigma^+,\ {}^2\Delta,\ {}^2\Delta^- \qquad (12a)$$

The symbol $2s\sigma$ used in (12) indicates small participation in the C−H bonds, which is probably correct for the free CH radical. Similarly in (12*a*), $(2q^+\sigma)$ is nearly but not entirely free from C−H bonding. Insofar as (12*a*) is needed for the formation of actual C_2H_2, the reorganization from (12) toward (12*a*) involves an increased participation of $2s\sigma$ (as part of $2q^-\sigma$) in the C−H bonds.

The fact that C_2H_2 acts as a weak acid indicates that there is a considerable net positive charge on each H atom, more so than in C_2H_4 or C_2H_6. This may well be connected with a reluctance of the carbon $2s$ electrons to enter into C−H homopolar bonds, because their natural I is so much greater than that of $1s$ of H. The importance of this effect is greater here than in C_2H_4 and especially C_2H_6, because a larger fraction of the C−H bonding is here taken care of by orbitals which (in LCAO approximation) are built up from carbon $2s$ orbitals.

Because of uncertainty as to the extent and effect of $s\sigma-p\sigma$ hybridization, and of $2s\leftrightarrow2s$ resonance, estimates of I's for the σ orbitals in (11) are decidedly uncertain. If we follow the usual rules and methods,[2,3] a good prediction can, however, be made for $(\pi+\pi,\pi_u)$, which is localized in the C−C bond region. We have

$$I(\pi+\pi)>I^\circ(2p\pi),$$

where $I°(2p\pi)$ for carbon is 10.86 volts, as determined in the usual way.[3] [This value differs a little from the value 11.23 volts for $2p\sigma$ and from the value 11.21 volts used for $2p_x$, $2p_y$ and $2p_z = 2p\sigma$ in discussing C_2H_4.] Allowing +2.5 volts for the inequality sign (cf. the corresponding case of N_2,[3a] where the inequality is +2.8 volts for $(\pi+\pi)$), and −1.5 volts as an estimate of the effect of the net negative charge on the carbons (polarities $H^+C^-C^-H^+$), one arrives at a prediction of about 11.9 volts for I of $(\pi+\pi)$.

The best experimental value of I for C_2H_2 probably is 11.35 volts, that obtained by Price from two Rydberg series. This is supported by a recent electron impact value 11.2 volts[16] (Morris[10] got 12.2). A comparison with our estimated I's makes it probable that the electron ionized is $(\pi+\pi)$, although the possibility $(\sigma+\sigma)$ or even $(s-s)$ cannot thereby be entirely excluded in view of the uncertainties as to the exact nature of these. Price's I is of course an adiabatic value; since a bonding electron is removed, the vertical I should be larger, but probably not much larger since only one C−C bonding electron out of six is removed. The fact that Price's Rydberg series bands are shaded toward the red indicates an increased moment of inertia in the upper states, in agreement with what we expect for excitation of a bonding electron. A reasonable guess for the vertical I would be 11.6 volts, in good agreement with our estimate given above for $(\pi+\pi)$.

We may next seek to interpret the observed ultraviolet absorption spectra of C_2H_2, namely, the relatively very weak band system λ2400–1900,[15, 17] and the Rydberg series of Price. According to Kistiakowsky, each band has a double head, presumably a Q and an R head, in which case the upper level is probably of type $^1\Pi_u$. Jonesco, however, using high resolution, finds that the bands (or at least several of them) have only P and R branches, with alternating intensities, exactly as expected if they are $^1\Sigma^+_g \rightarrow {}^1\Sigma^+_u$. This work also shows that the molecule is linear in the excited state, and that the moment of inertia is somewhat greater than in the normal state.

There appears to be some doubt, however, and some disagreement between Kistiakowsky and Jonesco, in regard to the vibrational analysis and the relative intensities of the bands. If the resultant vibrational states involved in the bands analyzed by Jonesco should be other than of the most symmetrical (Σ_g) type, then we could not conclude from the band structure that the electron transition is $^1\Sigma^+_g \rightarrow {}^1\Sigma^+_u$. The presence of vibrations of types ν_1 and ν_2, which are both of symmetry σ_g, also even certain combinations or harmonics of ν_3, ν_4, ν_5 (respectively of symmetry types σ_u, π_u and π_g), would, however, not invalidate the conclusion that the upper state is $^1\Sigma^+_u$, which on the whole seems the most probable. A possibility, however, suggested by the weakness of the bands, is that the electron transition is of a forbidden type.[11a] For certainty, a more complete analysis will be needed.

If the upper level of the λ2200 bands is $^1\Sigma^+_u$, this must probably be the $^1\Sigma^+_u$ of

$$(\pi+\pi, \pi_u)^{-1}(\pi-\pi, \pi_g), \ ^3,{}^1\Sigma^+_u, \ ^3,{}^1\Sigma^-_u, \ ^3,{}^1\Delta_u. \quad (13)$$

This assumption yields a term value of about 5 or 5.5 volts for $(\pi-\pi)$. If, however, the upper level should be $^1\Pi_u$, this must probably be $^1\Pi_u$ of

$$(\pi+\pi, \pi_u)^{-1}(3s\sigma_g), \ ^1,{}^3\Pi_u. \quad (14)$$

Here, similarly to C_2H_4 and C_2H_6, $3s$ corresponds to $(3s_{CH}+3s_{CH}, \sigma_g)$. The term value of 5 or 5.5 volts appears rather too high for $3s$, and the low intensity of the bands (only about 1/100,000 as strong as the Rydberg series bands according to Price) tends against this possibility. On the whole, it appears very probable that (13) rather than (14) is correct. That $(\pi-\pi)$ should be the lowest excited orbital of C_2H_2 is in harmony with what is known about the excited orbitals of N_2, NO, O_2 and C_2H_4. That the transition $(\pi+\pi)\rightarrow(\pi-\pi)$, involved in going from the normal state to $^1\Sigma^+_u$ of (13), is very weak is in agreement with what is known of the N_2 spectrum, and with the low intensity of $[x+x]\rightarrow[x-x]$ in C_2H_4.

As for Price's Rydberg series bands, the presence of probably only R heads in one series (I) gives evidence that here the upper electron levels are of Σ^+ type, presumably $^1\Sigma^+_u$, while the presence of double heads, presumably Q and R, in the other (II) indicates that there they are of Π type, presumably $^1\Pi_u$. It appears doubtful, however, that we can count on these results without a more detailed analysis, especially since it is stated that all the observed bands of each series

[16] J. T. Tate, P. T. Smith and A. L. Vaughan, Phys. Rev. **43**, 1054 (1933).

[17] G. B. Kistiakowsky, Phys. Rev. **37**, 277 (1931); G. Herzberg, Trans. Faraday Soc. **27**, 379 (1931). A. Jonesco, Comptes rendus **199**, 710 (1934); **200**, 817 (1935).

have the same kind of heads, a result which is inconsistent with the vibrational analysis given by Price.

Tentatively accepting the evidence for $^1\Sigma^+_u$ and $^1\Pi_u$ states, however, the following possibilities of explanation are available:

$$\begin{aligned} &\text{Series I:} \quad {}^1\Sigma^+_u \text{ of } (\pi+\pi,\ \pi_u)^{-1}(nx\pi_g),\ {}^{3,}\,{}^1\Sigma^+_u,\ {}^{3,}\,{}^1\Sigma^-_u,\ {}^{3,}\,{}^1\Delta_u. \\ &\text{Series II:} \quad {}^1\Pi_u \text{ of } (\pi+\pi,\ \pi_u)^{-1}(nx\sigma_g),\ {}^{3,}\,{}^1\Pi_u \text{ or of } (\pi+\pi,\ \pi_u)^{-1}(nx\delta_g),\ {}^{3,}\,{}^1\Pi_u,\ {}^{3,}\,{}^1\Gamma_u \end{aligned} \tag{15}$$

The only likely possibility for the excited orbital $nx\pi_g$ of series I is $nd\pi_g$ ($n=3, 4, \cdots$ for the observed bands). Now as Price points out, the λ2200 bands fit very well, so far as frequency is concerned, as $n=2$ of series I. This may well be significant, since the LCAO form $(\pi-\pi)$ in (13) closely resembles the atomic orbital $3d\pi$; it seems reasonable that $(\pi-\pi)$ may take the place of $3d\pi$, and so fit in as the first member of the $nd\pi$ series (the n numbering given by Price must then be increased by one). The low intensity for the λ2200 bands as compared with the others would then be somehow connected with the fact that $(\pi-\pi)$, unlike the other $nd\pi$, is not mostly outside the core. The existence of this sort of distinction is supported by empirical evidence in various other cases.

For series II the possibilities $ns\sigma_g$ or $nd\sigma_g$ and $nd\delta_g$ may be considered, with $nd\sigma$ ($n=3, 4, 5, \cdots$) the most likely; the term values are not reasonable for ns.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Critical Voltage for the Formation of Ozone by the Alternating-Current Discharge

In a study of the oxygen-ozone equilibrium condition with the same type of apparatus that was used in the study of active hydrogen,[1] it was found that the yield of ozone increased regularly with the voltage up to 75 volts on the primary. At this voltage the discharge was a faint bluish glow. Upon attempting to increase the voltage the discharge changed to a greenish-yellow glow. This was accompanied by a drop in voltage and an increase in amperage and wattage. The yield of ozone decreased and finally reached zero.

The gas stream was diverted from the potassium iodide absorption flask until the glowing discharge was well established, then the oxygen-ozone mixture was passed through the absorption flask for half an hour without producing a trace of free iodine. In Table I is a typical series of 15-minute runs at 1.5 liters per hour and at 25 mm pressure.

In run No. 7 the greenish-yellow glow appeared in the discharge 8 mm after the beginning of the run. In runs No. 9 and 10 the glow was present throughout the duration of the run.

The spectrograph showed the greenish-yellow glow to be composed of continuous spectrum in the red, yellow and green while oxygen bands appeared in the discharge proper. It would seem that conditions in the discharge should be just as favorable for producing ozone after the greenish-yellow glow appears as before when there is but a slight bluish glow around the electrodes.

TABLE I.

No.	Primary wattage	Primary voltage		Primary amperage	Percent of ozone by weight
1	7.5	45		1.4	0.76
2	10	50		1.6	0.94
3	11.2	55		1.8	1.06
4	13.7	60		2.	1.24
5	15.8	65		2.1	1.32
6	18	70		2.3	1.50
7	20	75		2.5	1.67
8	20	75	Glow appeared	2.5	0.90
9	35	65		3	.00
10	60	60		3.3	.00

For each fixed velocity and pressure there is a critical discharge voltage at which the greenish-yellow glow appears and ozone ceases to be formed. This problem is being investigated further.

M. SENKUS
A. C. GRUBB

Department of Chemistry,
University of Saskatchewan,
Saskatoon, Saskatchewan, Canada,
July 16, 1935.

[1] A. C. Grubb and A. B. Van Cleave, *Active Hydrogen*, J. Chem. Phys. **3**, 139 (1935).